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Activation and Reactions of Si-Si and Si-Ge σ-Bonds by Bis(t-alkyl isocyanide)palladium(0) Complexes(Dissertation_全文)

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Hideaki Oike

1996

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Preface

The studies presented in this thesis have been carried out under the direction of Professor Yoshihiko Ito at Kyoto University during 1993-1996. The studies are concerned with activation and reactions of Si–Si and Si–Ge σ-bonds by bis(*t*-alkyl isocyanide)palladium complexes.

The author wishes to express his sincerest gratitude to Professor Yoshihiko Ito for his constant guidance, valuable suggestions, and hearty encouragement through out this work. The author is deeply grateful to Dr. Michinori Suginome for his continuous advice and helpful discussions during course of this work. The author is also indebted to Associate Professor Masahiro Murakami, Dr. Masaya Sawamura, and Professor Kohei Tamao for their helpful suggestions. The author is fortunate to have had the great assistance of Messrs. Mitsuru Sugawara, Sang-Soo Park, Miss Philippa H. Shuff, and Mr. Nobuhiko Takeda.

The author is deeply grateful to Professor Tatsuya Shono who led the author to chemistry during 1991-1993. The author is thankful to Dr. Naoki Kise and other members of Prof. Shono's group for their kind considerations.

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The author wishes to thank to Dr. Eiji Ihara, Dr. Hitoshi Hamashima, and Dr. Minoru Hayashi for their kind advice. The author is thankful to Messrs. Hideki Amii, Hajime Ito, Ryoichi Kuwano, Hiroshi Nakamura, Takafumi Ohara, and Akira Matsumoto for their kindness and good will in carrying out this work. Furthermore, he is sincerely grateful to Miss Chiyo Nagae and other members of Prof. Ito's research group for their kind encouragement.

The author thanks the Shin-Etsu Co. Ltd. and ASAI Germanium Research Institute for the donation of various chlorosilanes and germanium tetrachloride, respectively.

Finally, the author express his deep appreciation to his family, especially his father, Mr. Yusai Oike and his late mother, Mrs. Mihoko Oike for their constant assistance and encouragement.

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Kyoto University
1996

Contents

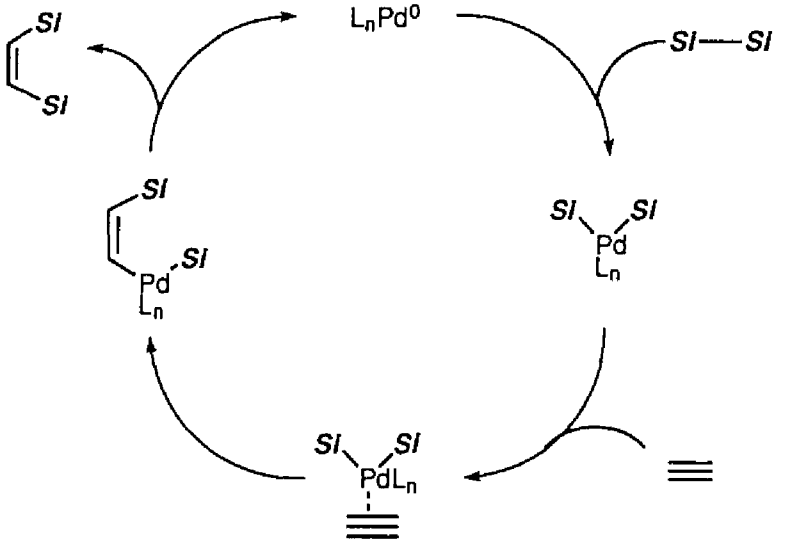
General Introduction

Today, in the field of organic chemistry as well as material science, group 14 organometallic compounds, especially organosilanes play an important role. For synthetic chemists, various selective transformations of organosilicon reagents have been useful and attractive in the construction of complex molecules.[1] On the other hand, organosilicon polymers containing silicon–silicon bonds in which *sigma* electrons delocalize have been of great interest in material science because of their unique chemical and physical properties.[2] Furthermore, the chemistry of silicon has been extended to germanium chemistry due to its close proximity to silicon in the periodic table. Therefore, the development of new methods for the selective formation of silicon–carbon and silicon–silicon bonds has become more and more desirable. From this point of view, transition metal catalyzed reactions provide a new pathway to many organosilicon and related organogermanium compounds. In the coordination sphere of transition metals, the formation and cleavage of silicon–element bonds occur under mild conditions.

Over the past two decades, considerable attention has been focused on the palladium-catalyzed addition of Si–Si bonds to unsaturated compounds, *i.e.*, bis-silylation, which forms two silicon–carbon bonds simultaneously.[3] The reaction is considered to proceed through the mechanism shown in Scheme 1 for acetylene. The steps included are : (1) oxidative addition of the Si–Si bond to palladium(0), forming bis(organosilyl)palladium(II), (2) formation of a π-complex with acetylene, (3) insertion of the acetylene into one of the palladium–silicon bonds, and (4) reductive elimination of the bis-silylated product.

In early investigations, reactive disilanes bearing electron-withdrawing groups or strained cyclic disilanes were required to obtain bis-silylated products in high yields. Since the calculated heat of reaction for the formation of bis(organosilyl)alkenes from substituted disilanes and acetylenes is ca. -40 kcal/mol,[4] even peralkylated (non-activated) disilanes should give products if a kinetically favored reaction pathway is developed. In spite of many efforts, however, it was difficult to activate Si–Si bonds of such disilanes using conventional palladium–phosphine catalysts. Moreover, bis-silylation of alkenes was hardly achieved.

Scheme 1.



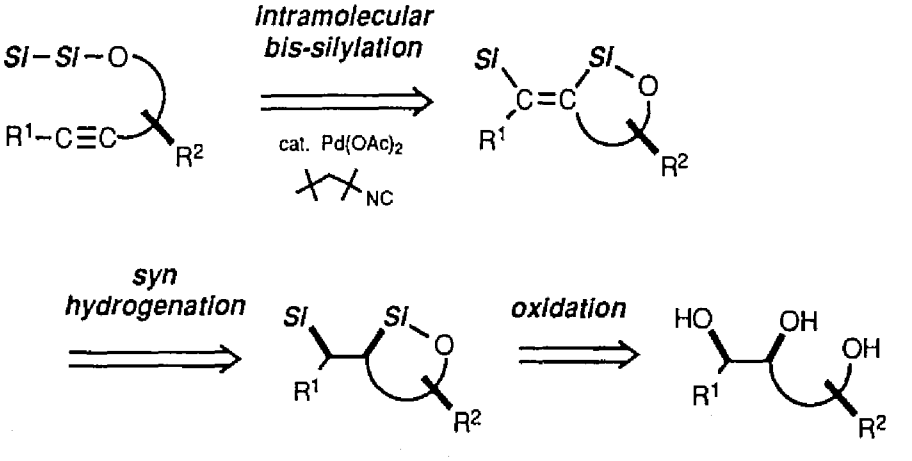
During the last five years, much progress has been made in many aspects of this field. In 1991, Ito and co-workers developed a novel palladium–isonitrile catalyst that was active in the bis-silylation of terminal acetylenes with unreactive disilanes.[5] Tanaka, et al. also reported independently, that a palladium–phosphite catalyst was also effective for bis-silylation of terminal acetylenes.[6] This palladium–isonitrile catalyst, furthermore, possessed high activity for intramolecular bis-silylation of alkenes.[7] In addition to the development of these highly active catalysts, several mechanistic details of bis-silylation were clarified by the synthesis and isolation of the bis(organosilyl)palladium(II) complexes suggested as intermediates. In 1992, Fink, et al. reported the first fully characterized bis(organosilyl)palladium(II) complex that reacted with dimethyl acetylenedicarboxylate to give the corresponding bis-silylated olefin.[8] In 1994, Murakami, Ito and co-workers also demonstrated a mechanistic model of catalytic bis-silylation of acetylenes using an isolable bis(organosilyl)palladium(II) complex.[9] Though these bis(organosilyl)palladium(II) complexes were too stable to act as catalysts of bis-silylation themselves, they evidenced some important steps of the catalytic cycle of bis-silylation.

Transition metal catalyzed disilane metathesis also seemed very attractive for the selective formation of silicon–silicon bonds. To the author's best knowledge, however, only a few examples of metathesis have been reported. In 1976, Tamao,

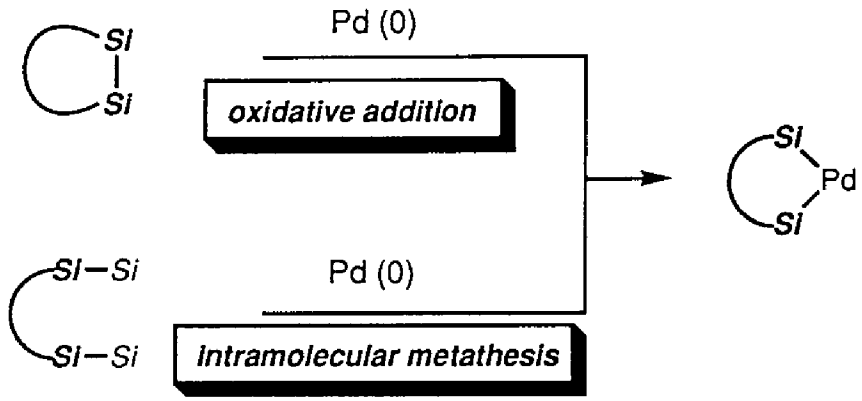
Hayashi and Kumada found that the metathesis reaction of 1,1,2,2-tetramethyl-1,2-disilacyclopentane proceeded at high temperature in the presence of a palladium–phosphine catalyst to give a cyclic dimer in 39% yield.[10] Although Ando and co-workers also reported metathesis dimerization of highly strained cyclic disilanes in high yield,[11] no higher cyclic oligomer than the cyclic dimer was obtained in these investigations.

The silicon–silicon σ-bond activation, which is commonly involved as a crucial step for the bis-silylation as well as metathesis, has not been extensively studied for synthetic applications due to the lack of highly active transition metal catalyst. Similarly, the activation of the silicon–germanium σ-bond has not been investigated and palladium– and platinum–organogermanium complexes have not been fully characterized so far. Hence, the author wishes to describe his efforts investigating reactions involving the activation of silicon–silicon and –germanium σ-bonds by bis(*t*-alkyl isocyanide)palladium(0) complexes.

Chapter 1 describes intramolecular bis-silylation of carbon–carbon triple bonds leading to stereoselective synthesis of 1,2,4-triols. Various terminal and internal alkynes tethered to disilanyl groups underwent the intramolecular bis-silylation in the presence of *t*-alkyl isocyanide–palladium complex to give exocyclic 1,2-oxasilolanes in high yields. 1,2,4-Triols were obtained by stereoselective hydrogenation of the C–C double bonds and subsequent stereospecific oxidative transformation of the Si–C bonds into hydroxy groups.

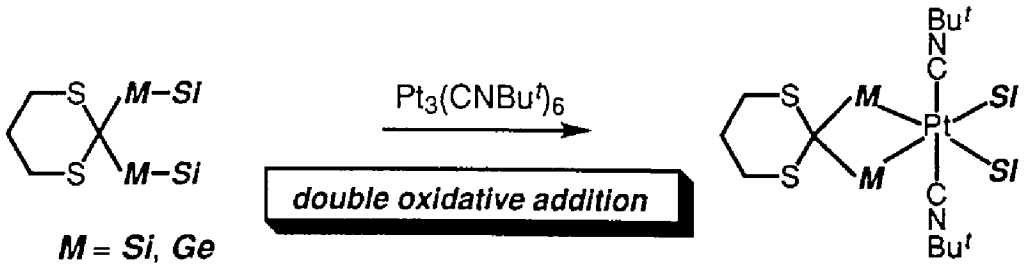


Chapter 2 deals with the synthesis and reactions of cyclic bis(organosilyl)palladium complexes. 4- to 7- Membered cyclic bis(organosilyl)-palladium complexes were synthesized by two different methods. The first, by oxidative addition of cyclic disilanes onto bis(*t*-butyl isocyanide)palladium(0) complex and the second, by intramolecular metathesis of the two Si–Si σ-bonds of bis(disilane)s by palladium(0) complex.

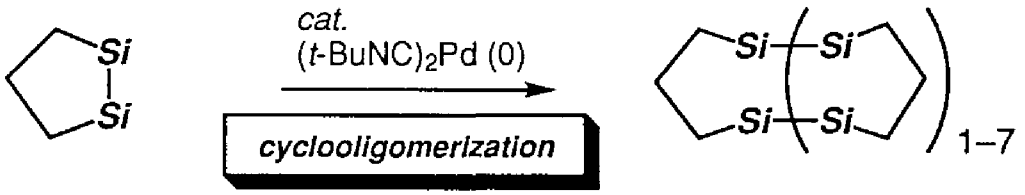


The reactivities of the cyclic bis(organosilyl)palladium complexes toward cyclic disilanes, phosphines, and alkynes were also examined. Furthermore, new catalytic bis-silylation involving the cyclic bis(organosilyl)palladium intermediates generated by the intramolecular metathesis was developed.

Chapter 3 describes the reactions of bis(disilanyl)dithiane and bis(silylgermyl)dithiane with isonitrile complexes of platinum(0) and palladium(0). Tetrakis(organosilyl)platinum(IV) and bis(organogermyl)bis(organosilyl)-platinum(IV) complexes were obtained by double oxidative addition of Si–Si and Si–Ge σ-bonds onto a platinum(0) complex, respectively. Bis(*t*-butyl isocyanide)palladium(0) also mediated intramolecular Si–Ge σ-bond metathesis to afford a cyclic bis(organogermyl)palladium(II) complex, whose structure was determined by a X-ray diffraction study.



Chapter 4 is concerned with palladium-catalyzed oligomerization of cyclic disilanes through Si–Si σ-bond metathesis. Cyclic oligomers up to the 40-membered octamer were isolated by the ring-enlargement oligomerization of 1,1,2,2,-tetramethyl-1,2-disilacyclopentane.



Reactions with the dimer, trimer, and tetramer in the presence of a stoichiometric and catalytic amount of bis(*t*-butyl isocyanide)palladium(0) complex revealed that this oligomerization proceeded by a reversible mechanism between the monomer and oligomers. Furthermore, new macrocyclic organosilicon compounds were synthesized from the cyclic oligomers by the elaboration of the Si–Si linkages of the oligomers.

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Chapter 1

Stereoselective Synthesis of 1,2,4-Triols via Intramolecular Bis-Silylation of Carbon–Carbon Triple Bonds Followed by Hydrogenation

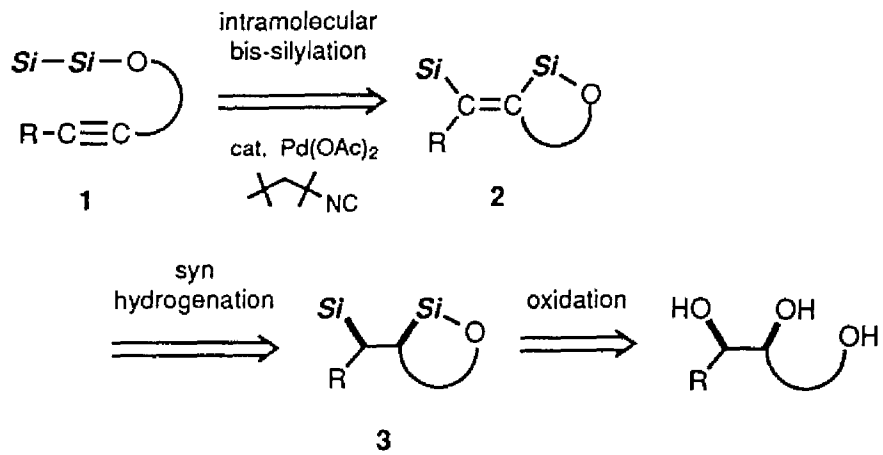
Abstract: A new strategy for the stereoselective synthesis of 1,2,4-triols has been developed. An alkyne tethered to a disilanyl group, upon treatment with palladium acetate and *t*-alkyl isocyanide, furnished an exocyclic bis-silylated olefin. Subsequent hydrogenation took place selectively from the less-hindered side of the ring, producing *cis*-disubstituted oxasilolane. Oxidation of the two C–Si bonds of the hydrogenated oxasilolane led to the stereo- and regio-defined synthesis of 1,2,4-triol.

Introduction

The development of new synthetic strategies for stereoselective construction of polyol skeletons has been an active area of research in recent years. Stereoselective formation of C–Si bonds is one of the promising approaches to the polyol synthesis,[1] since oxidation of C–Si bonds gives rise to hydroxyl groups with retention of stereochemistry.[2] In the previous reports, Ito and co-workers have been studying bis-silylation of unsaturated organic molecules,[3,4] and developed a highly efficient catalyst system, palladium(II) acetate / *t*-alkyl isocyanide, for the inter- and/or intramolecular bis-silylation of C–C triple[3c,f] and double[3d,e,g,h] bonds. Intramolecular regioselective bis-silylation reaction of an alkyne tethered to a disilanyl group **1** produces an exocyclic olefin **2**, which is derived from *syn* addition of the two silicon atoms across the triple bond. The following *syn* addition of hydrogen to the C–C double bond of **2** would stereoselectively create two asymmetric centers each having

a silicon atom, which constitute a potential precursor for a vicinal diol unit. Herein, the author reports the details of the stereoselective synthesis of 1,2,4-triols by intramolecular bis-silylation of C–C triple bonds and subsequent hydrogenation as envisioned in Scheme 1.

Scheme 1.

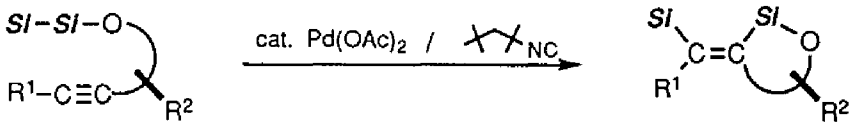


Results and Discussion

Synthesis of Alkynes Tethered to Disilanyl Groups 1. Alkynes tethered to disilanyl groups through silyl ether linkage **1** were readily prepared in good yield by the reaction of acetylenic alcohols with chlorodisilanes in the presence of amines in tetrahydrofuran (THF) or in *N,N*-dimethylformamide (DMF). An alkyne linked to a disilanyl group through a carbon chain **1h** was prepared by the reaction of an acetylenic Grignard reagent with a chlorodisilane in THF.

Intramolecular Bis-Silylation of C–C Triple Bonds. A mixture of a disilanyl alkyne **1**, palladium(II) acetate (0.007–0.02 equiv), and 1,1,3,3-tetramethylbutyl isocyanide (0.1–0.3 equiv) in toluene was heated under the conditions specified in Table 1. The Si–Si linkage added intramolecularly to the C–C triple bond and, except entry 15, this addition was totally exo and *syn*,[5] as is the case with an intermolecular variant,[3c,4] to afford a bis-silylated exocyclic olefin **2** in good yield. Although the catalyst is potentially effective for the intermolecular bis-silylation of terminal alkynes,[3c] those **1a–e** reacted only intramolecularly giving the corresponding

Table 1. Intramolecular Bis-Silylation of **1**



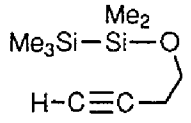
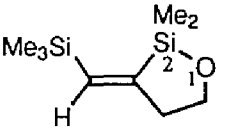
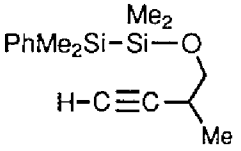
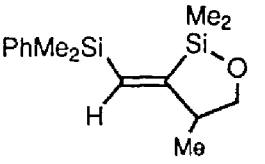
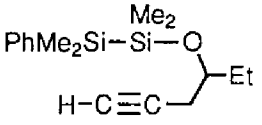
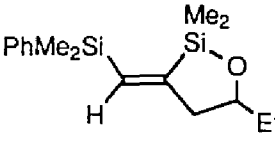
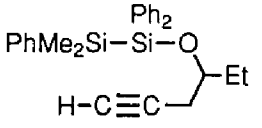
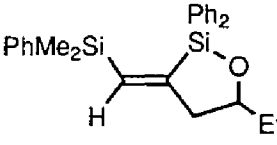
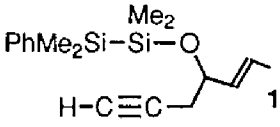
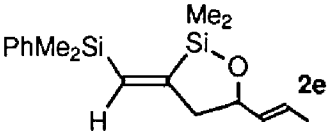
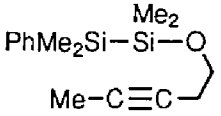
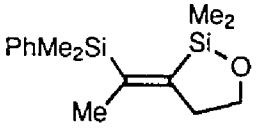
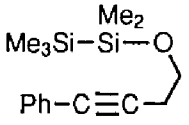
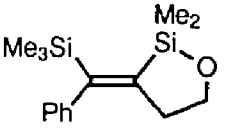
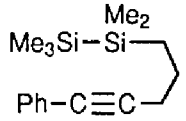
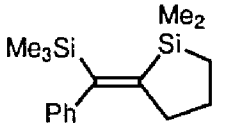
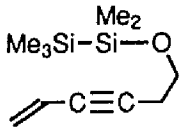
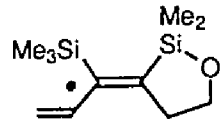
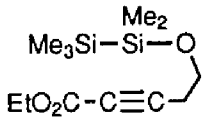
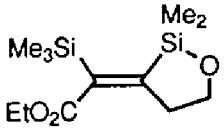
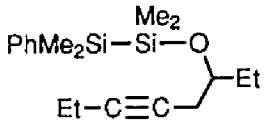
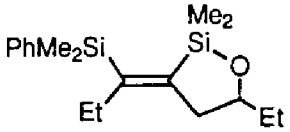
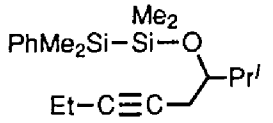
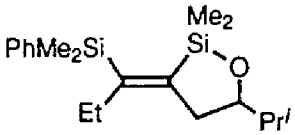
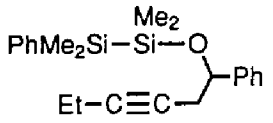
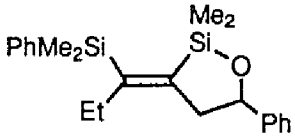
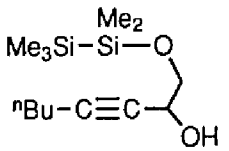
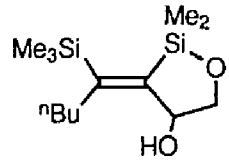
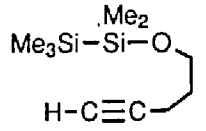
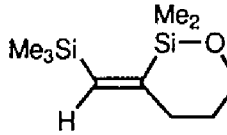
entry	1	conditions	product 2	yield, %
1	 **1a**	80 °C 6 h	 **2a**	91
2	 **1b**	80 °C 2.5 h	 **2b**	56
3	 **1c**	60 °C 13 h	 **2c**	96
4	 **1d**	70 °C 12 h	 **2d**	99
5	 **1e**	50 °C 23 h	 **2e**	75
6	 **1f**	80 °C 1 h	 **2f**	94
7	 **1g**	111 °C 2 h	 **2g**	85
8	 **1h**	111 °C 1 h	 **2h**	85

Table 1. (continued)

entry	1	conditions	product 2	yield, %
9	 **1l**	80 °C 2 h	 **2l**	81
10	 **1j**	80 °C 3 h	 **2j**	97
11	 **1k**	70 °C 15 h	 **2k**	93
12	 **1l**	100 °C 6 h	 **2l**	97
13	 **1m**	70 °C 8 h	 **2m**	82
14	 **1n**	60 °C 9 h	 **2n**	96
15	 **1o**	100 °C 10 h	 **2o**	71 [a]

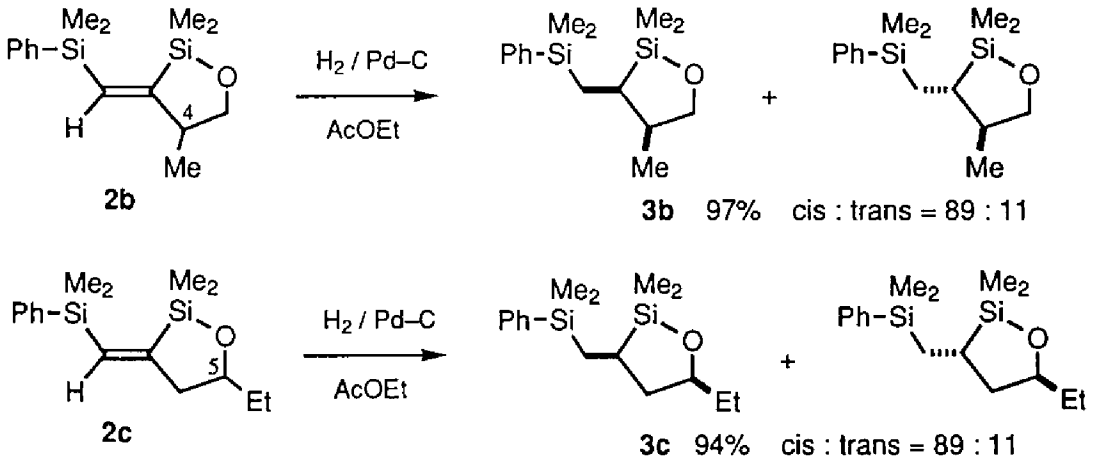
[a] A mixture of (*Z*)- and (*E*)- isomers (88 : 12)

cyclic 1,2-oxasilolanes **2a–e** (entries 1–5). Furthermore, the high activity of the present catalyst system, combined with an advantage of intramolecular reaction, rendered it possible to insert an *internal* C–C triple bond into Si–Si linkage (entries 6–

14). In comparison with terminal alkynes, intermolecular bis-silylation of internal alkynes is scarce.[4] The internal C–C triple bonds in conjugation with an ester or an olefin underwent the chemoselective bis-silylation (entries 9, 10). The intramolecular bis-silylations of alkynes **1** bearing various substituents in the tether worked as well, affording the corresponding oxasilolanes **2** with an asymmetric center in the ring. It may be remarked that a propargylic hydroxyl group does not encumber the desired bis-silylation (entry 14). Reaction employing a terminal alkyne tethered to a disilanyl group by a chain of 4 atoms produced a mixture of (*Z*)- and (*E*)-isomers (88 : 12) of 6-membered adducts (entry 15). However, bis-silylation failed to proceed with an internal alkyne tethered to a disilanyl group by a chain of 4 atoms.

Hydrogenation of the Bis-Silylated Products 2. Catalytic hydrogenation of the 1,2-oxasilolanes **2b** and **2c** having asymmetric centers on 4- and 5-positions of the rings, respectively, was carried out using Pd on carbon under an atmospheric pressure of hydrogen in AcOEt at room temperature (Scheme 2). In both cases, addition of hydrogen to the C–C double bond occurred from the less-hindered side of the ring to give *cis*-disubstituted oxasilolanes with fair diastereoselection.[6]

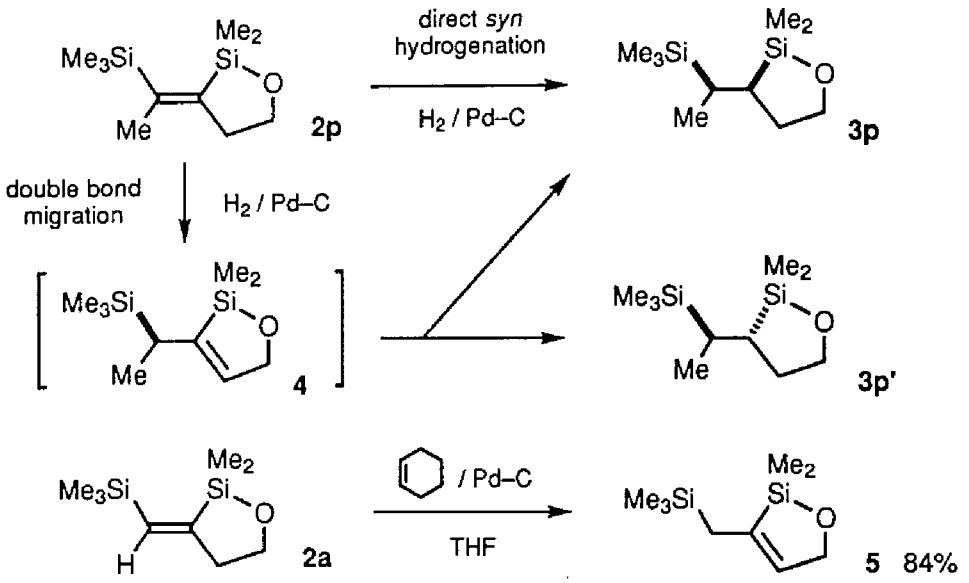
Scheme 2.



Next, a 1,2-oxasilolane **2p** prepared from an internal alkyne[3c] was hydrogenated, stereospecific formation of **3p** being expected from a *syn* hydrogenation mechanism. However, catalytic hydrogenation of the tetra-substituted olefin **2p** was slower than that of tri-substituted olefins **2b** and **2c**, and produced 1:1 mixture of **3p**

and an unexpected isomer **3p'** (Scheme 3). It may be presumed that double bond migration of **2p** takes place prior to, or in competition with, direct hydrogenation and that hydrogenation of the resulting endocyclic olefin **4** proceeds non-stereoselectively affording a mixture of **3p** and its stereoisomer **3p'**. An analogous double bond migration to an endocyclic olefin **5** was observed when **2a** was treated with Pd on carbon in the presence of cyclohexene. This result supports the involvement of double bond migration in the catalytic hydrogenation process.

Scheme 3.

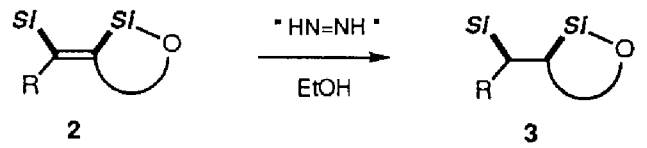


Stereospecific *syn* hydrogenation of tetra-substituted olefins **2f,k–m** could be achieved by means of diimide reduction (Table 2). Diimide, generated *in situ* by acid treatment of potassium azodicarboxylate, reduced **2f** to give the *syn*-hydrogenated product **3f** exclusively, presumably by a cyclic mechanism.[7] In the diimide reduction of **2k–m** having an asymmetric center in the oxasilolane ring, *syn* addition of hydrogen to the C–C double bond took place preferentially from the less-hindered side of the ring like the catalytic hydrogenation using Pd on carbon.[6] Of note was that two asymmetric centers were stereoselectively created in **3k–m** at once.

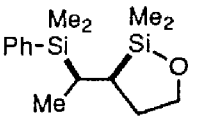
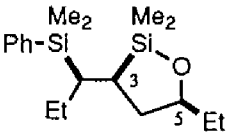
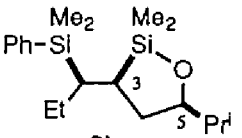
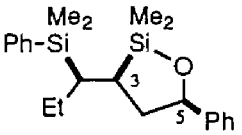
Diimide reduction was also conducted with the acyclic substrate alkene **6** prepared by ring opening reaction of the oxasilolane **2m** with phenyllithium (Scheme 4). In marked contrast to the cyclic substrate **2m**, the acyclic **6** resulted in poor selectiv-

ity together with poor yield, suggesting the advantages of the cyclic system of the oxasilolane.

Table 2. Hydrogenation of Tetra-substituted Olefins with Diimide

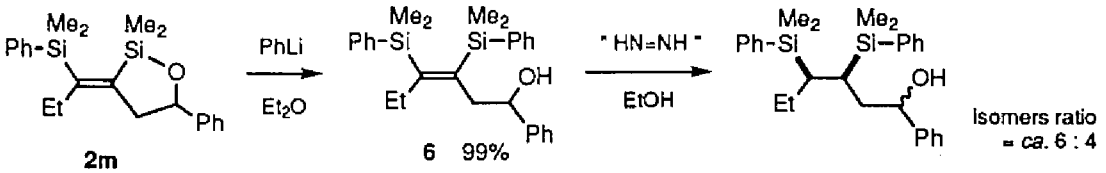


2 3

entry	2	major product	cis : trans [a] (yield, %)
1	2f	 3f	— (99)
2	2k	 3k	85 : 15 (97)
3	2l	 3l	88 : 12 (98)
4	2m	 3m	92 : 8 (99)

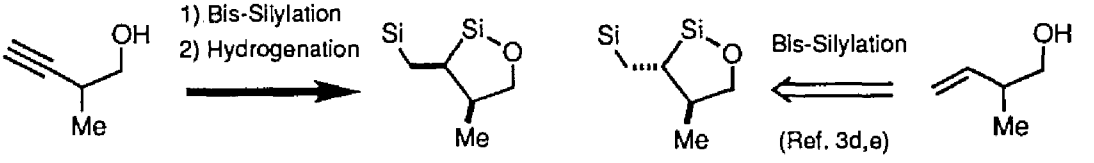
[a] Referring to the relationship between the 3- and 5-substituents of the 1,2-oxasilolane.

Scheme 4.



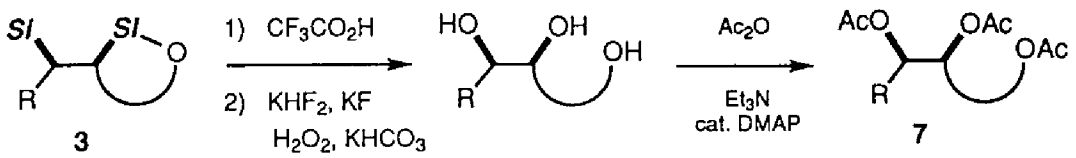
As previously reported in Ito's paper,[3d,e] the intramolecular bis-silylation of ***alkenes*** also stereoselectively furnishes oxasilolanes and the alkene having an allylic substituent leads to the ***trans***-3,4-disubstituted oxasilolane. On the other hand, the present intramolecular bis-silylation of an ***alkyne*** bearing a propargylic substituent followed by hydrogenation gave rise to the corresponding ***cis***-3,4-disubstituted oxasilolane (Scheme 5). Thus, the present stereoselective synthesis of oxasilolanes gives synthetically useful features complementary to the intramolecular bis-silylation of alkenes.[3d,e]

Scheme 5.

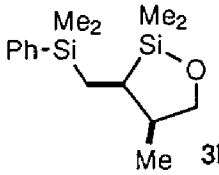
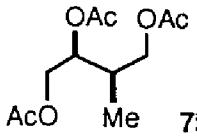
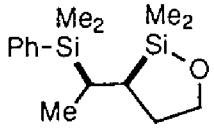
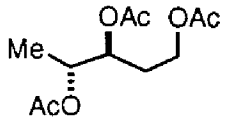
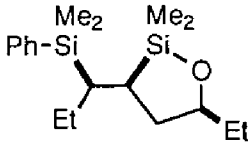
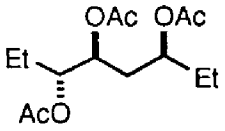
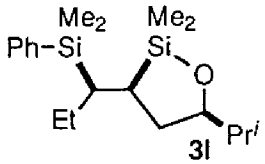
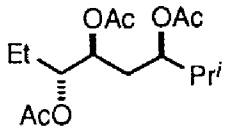
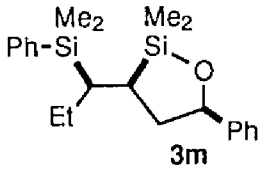
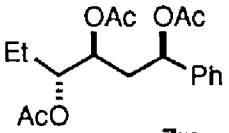


Oxidation of the Hydrogenated Products 3 into 1,2,4-Triols. The oxasilolanes **3b,f,k–m**, bearing dimethylphenylsilyl groups feasible for the oxidative transformation into hydroxyl groups,[2d,e] were subjected to the oxidation procedure (Table 3). The Ph–Si bonds of **3b,f,k,l** were cleaved by treatment with trifluoroacetic acid[2e] and subsequent hydrogen peroxide oxidation in the presence of fluoride anion[2c] afforded the corresponding 1,2,4-triols with retention of stereochemistry. With **3m**, the Ph–Si bond was cleaved by treatment with potassium *t*-butoxide in dimethyl sulfoxide (DMSO)[8] to prevent Friedel-Crafts type migration of the phenyl group on the silicon (entry 5).[2d,9] The 1,2,4-triols thus produced were acetylated to allow an isolation affording the triacetates **7** in moderate to good yield.

Table 3. Synthesis of 1,2,4-Triols by Oxidation of Oxasilolanes **3**



3 **7**

entry	**3**	product [a]	yield, %
1	 **3b**	 **7b**	97
2	 **3f**	 **7f**	86
3	 **3k**	 **7k**	57
4	 **3l**	 **7l**	56
5	 **3m**	 **7m**	78 [b]

[a] A mixture of stereoisomers of **3** was oxidized and the produced major isomer is shown.

[b] Oxidation: 1) $KOBu^t$ / DMSO. 2) TBAF, $KHCO_3$, H_2O_2.

Conclusion

A carbon–carbon triple bond was stereoselectively transformed to a vicinal diol unit through the intramolecular bis-silylation, hydrogenation, and oxidation. This procedure, creating two asymmetric centers, provides a novel method for stereoselective synthesis of 1,2,4-triols. Of note is that the present method offers a new synthetic means complementary to the intramolecular bis-silylation of carbon–carbon double bonds.[3d,e]

Experimental Section

General and Materials. Column chromatography was performed with silica gel (Wakogel C-200). ^1H and ^{13}C NMR spectra were acquired in chloroform-*d* unless otherwise noted. Carbon chemical shifts were recorded relative to chloroform-*d* (δ 77.0). Where appropriate, NMR data only for the major stereoisomer were described. IR spectra were recorded with a Hitachi 270-30 spectrometer. Toluene was distilled from $LiAlH_4$, THF from sodium diphenylketyl, DMF, AcOEt and DMSO from CaH_2, and methanol from magnesium methoxide. Unless otherwise noted, materials were obtained from commercial sources. 2-Methylbut-3-yn-1-ol was prepared by the reaction of a propargylic titanium reagent with formaldehyde.[10] Hept-5-en-1-yn-4-ol was prepared by zinc mediated reaction of propargyl bromide with crotonaldehyde.[11] 4-Phenylbut-3-yn-1-ol and hex-5-en-3-yn-1-ol were prepared using Sonogashira procedure.[12] Ethyl 5-hydroxypent-2-ynoate was prepared by the reaction of a lithium acetylide with oxirane.[13]

Preparation of Disilanyl Alkynes 1. The following describes the general procedure for the synthesis of disilanyl alkynes **1a–c,e–g,i–k,n,o**. To a mixture of an acetylenic alcohol (4.3 mmol), Et_3N (6.4 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in THF (10 mL) at room temperature was added a chlorodisilane (4.3 mmol). Progress of the reaction was monitored by GC and/or TLC and, after completion, the mixture was diluted with hexane (10 mL). Filtration to remove salts and Kugelrohr distillation of the filtrate afforded **1**.

Disilanyl alkynes **1d,l,m** were prepared according to the following procedure. To a mixture of an acetylenic alcohol (5.7 mmol) and a chlorodisilane (5.7 mmol) in DMF (3.5 mL) at room temperature was added imidazole (11.4 mmol). The mixture was stirred at room temperature and, after completion, subjected to column chromatography to afford **1**.

A disilanyl alkyne **1h** was prepared as follows. To a solution of (5-phenyl-4-pentynyl)magnesium chloride (18.5 mmol) in THF (19 mL) at 0 °C was added chloropentamethyldisilane (3.3 g, 20 mmol). The mixture was stirred at room temperature for 2 h and at 50 °C for 1.5 h, cooled, and then slowly poured into aqueous HCl (1 N) at 0 °C. Extraction with ether followed by Kugelrohr distillation afforded **1h** (1.5 g, 30%).

(*Z*)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]-1,2-oxasilolane (2a). A toluene solution (3.5 mL) of $Pd(OAc)_2$ (6.6 mg, 29 μmol), 1,1,3,3-tetramethylbutyl isocyanide (62 mg, 0.45 mmol), and 4-[(pentamethyldisilanyl)oxy]-1-butyne (**1a**, 542 mg, 2.7 mmol) was heated at 80 °C for 6 h. Kugelrohr distillation [130–140 °C (20 mmHg)] of the cooled reaction mixture afforded **2a** (493 mg, 91%). IR (neat) 2964, 2908, 2868, 1252, 1068, 1030 cm^{-1}; ^1H NMR δ 0.11 (s, 9 H), 0.32 (s, 6 H), 2.65 (dt, J = 2.2, 6.5 Hz, 2 H), 3.94 (t, J = 6.5 Hz, 2 H), 6.57 (t, J = 2.2 Hz, 1 H); ^{13}C NMR δ -0.18, 0.30, 43.67, 64.83, 141.70, 159.81. Anal. Calcd for $C_9H_{20}OSi_2$: C, 53.93; H, 10.06. Found: C, 53.72; H, 10.18.

The following reactions for the synthesis of **2** were carried out according to the preceding procedure for **2a** under the conditions specified in Table 1.

(*Z*)-3-[(Dimethylphenylsilyl)methylene]-2,2,4-trimethyl-1,2-oxasilolane (2b). IR (neat) 2968, 1252, 1114, 1036, 850 cm^{-1}; ^1H NMR δ 0.10 (s, 3 H), 0.13 (s, 3 H), 0.40 (s, 6 H), 1.07 (d, J = 6.8 Hz, 3 H), 2.57–2.78 (m, 1 H), 3.47 (dd, J = 7.8, 9.2 Hz, 1 H), 4.09 (dd, J = 6.6, 9.2 Hz, 1 H), 6.59 (d, J = 2.3 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.50–7.59 (m, 2 H); ^{13}C NMR δ -0.63, -0.49, 0.70, 1.00, 16.74, 46.29, 72.01, 128.33, 129.62, 134.70, 137.71, 139.39, 167.21. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.10; H, 8.95.

(*Z*)-3-[(Dimethylphenylsilyl)methylene]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (2c). IR (neat) 2968, 1252, 1111, 836 cm^{-1}; ^1H NMR δ 0.11 (s, 6 H), 0.38 (s, 3 H), 0.39 (s, 3 H), 0.94 (t, J = 7.4 Hz, 3 H), 1.36–1.74 (m, 2 H), 2.43 (ddd, J = 2.4, 8.0, 15.0 Hz, 1 H), 2.73 (ddd, J = 1.8, 5.2, 15.0 Hz, 1 H), 3.82–3.98 (m, 1 H), 6.68 (dd, J = 1.8, 2.4 Hz, 1 H), 7.28–7.65 (m, 5 H); ^{13}C NMR δ -1.29, -1.12, 0.24,

0.55, 9.86, 30.61, 49.26, 76.76, 127.78, 129.08, 134.15, 138.83, 139.27, 162.85. Anal. Calcd for $C_{16}H_{26}OSi_2$: C, 66.14; H, 9.02. Found: C, 66.14; H, 9.22.

(*Z*)-3-[(Dimethylphenylsilyl)methylene]-5-ethyl-2,2-diphenyl-1,2-oxasilolane (2d). IR (neat) 3076, 2968, 1432, 1252, 1118, 840 cm^{-1}; ^1H NMR δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.94 (t, J = 7.4 Hz, 3 H), 1.45–1.85 (m, 2 H), 2.64 (ddd, J = 2.5, 8.4, 15.5 Hz, 1 H), 2.93 (ddd, J = 1.7, 5.3, 15.5 Hz, 1 H), 4.05–4.22 (m, 1 H), 6.92 (dd, J = 1.7, 2.5 Hz, 1 H), 7.19–7.69 (m, 15 H); ^{13}C NMR δ -1.71, -1.59, 9.87, 30.81, 49.99, 77.55, 127.64, 127.83, 128.78, 130.35, 133.22, 133.77, 135.63, 135.76, 138.96, 142.89, 158.12. Anal. Calcd for $C_{26}H_{30}OSi_2$: C, 75.31; H, 7.29. Found: C, 75.46; H, 7.37.

(*Z*)-3-[(Dimethylphenylsilyl)methylene]-2,2-dimethyl-5-(1-propenyl)-1,2-oxasilolane (2e). IR (neat) 2968, 1438, 1254, 1116, 842 cm^{-1}; ^1H NMR δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.36 (s, 3 H), 0.37 (s, 3 H), 1.69 (dd, J = 1.4, 6.4 Hz, 3 H), 2.53 (ddd, J = 2.6, 8.6, 15.4 Hz, 1 H), 2.69 (ddd, J = 1.6, 5.2, 15.4 Hz, 1 H), 4.27–4.41 (m, 1 H), 5.49 (ddd, J = 1.4, 6.8, 15.2 Hz, 1 H), 5.70 (dq, J = 15.2, 6.4 Hz, 1 H), 6.66 (dd, J = 1.6, 2.6 Hz, 1 H), 7.30–7.66 (m, 5 H); ^{13}C NMR δ -1.30, -1.12, -0.29, 0.41, 17.69, 50.33, 76.06, 127.04, 127.83, 129.15, 133.50, 134.20, 138.77, 139.51, 162.39. Anal. Calcd for $C_{17}H_{26}OSi_2$: C, 67.49; H, 8.66. Found: C, 67.23; H, 8.76.

(*Z*)-3-[1-(Dimethylphenylsilyl)ethylidene]-2,2-dimethyl-1,2-oxasilolane (2f). IR (neat) 2964, 1435, 1252, 1066, 1036, 934, 810 cm^{-1}; ^1H NMR δ 0.16 (s, 6 H), 0.40 (s, 6 H), 1.83 (t, J = 1.4 Hz, 3 H), 2.63 (tq, J = 6.6, 1.4 Hz, 2 H), 3.99 (t, J = 6.6 Hz, 2 H), 7.29–7.54 (m, 5 H); ^{13}C NMR δ -1.11, 0.56, 21.39, 36.11, 64.17, 127.35, 128.99, 134.17, 138.69, 146.21, 153.30. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.10; H, 8.97.

(*Z*)-2,2-Dimethyl-3-[phenyl(trimethylsilyl)methylene]-1,2-oxasilolane (2g). IR (neat) 3064, 2964, 2868, 1252, 1088, 1030 cm^{-1}; ^1H NMR δ 0.06 (s, 9 H), 0.42 (s, 6 H), 2.30 (t, J = 6.6 Hz, 2 H), 3.82 (t, J = 6.6 Hz, 2 H), 6.87–6.92 (m, 2 H), 7.12–7.21 (m, 1 H), 7.26–7.35 (m, 2 H); ^{13}C NMR δ -0.01, 0.69, 37.71, 64.64, 125.36, 126.69, 128.36, 146.77, 153.30, 156.57. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.13; H, 8.93.

(*Z*)-1,1-Dimethyl-2-[phenyl(trimethylsilyl)methylene]silolane (2h). IR (neat) 2948, 1598, 1250 cm^{-1}; ^1H NMR δ 0.04 (s, 9 H), 0.33 (s, 6 H), 0.70 (t, J = 7.0 Hz, 2 H), 1.53 (quintet, J = 7.0 Hz, 2 H), 1.99 (t, J = 7.0 Hz, 2 H), 6.82–6.89 (m, 2 H), 7.09–7.18 (m, 1 H), 7.23–7.32 (m, 2 H); ^{13}C NMR δ -0.27, 0.63, 15.86, 23.69, 39.54,

124.73, 126.87, 128.00, 147.52, 154.93, 157.81. Anal. Calcd for $C_{16}H_{26}Si_2$: C, 70.00; H, 9.54. Found: C, 70.09; H, 9.76.

(*Z*)-2,2-Dimethyl-3-[1-(trimethylsilyl)prop-2-enylene]-1,2-oxasilolane (2i). IR (neat) 2964, 1616, 1252, 1032 cm^{-1}; ^1H NMR δ 0.16 (s, 9 H), 0.35 (s, 6 H), 2.66 (dt, J = 1.4, 6.5 Hz, 2 H), 3.92 (t, J = 6.5 Hz, 2 H), 4.93 (dd, J = 2.0, 18.0 Hz, 1 H), 5.14 (dd, J = 2.0, 11.6 Hz, 1 H), 6.42 (ddt, J = 11.6, 18.0, 1.4 Hz, 1 H); ^{13}C NMR δ 0.70, 0.92, 37.03, 64.49, 114.83, 140.53, 151.97, 152.92. Anal. Calcd for $C_{11}H_{22}OSi_2$: C, 58.34; H, 9.79. Found: C, 58.08; H, 10.00.

(*Z*)-3-[(Ethoxycarbonyl)(trimethylsilyl)methylene]-2,2-dimethyl-1,2-oxasilolane (2j). IR (neat) 2968, 1716, 1254, 1200, 1094, 1032, 864 cm^{-1}; ^1H NMR δ 0.19 (s, 9 H), 0.37 (s, 6 H), 1.32 (t, J = 7.2 Hz, 3 H), 2.69 (t, J = 6.5 Hz, 2 H), 3.95 (t, J = 6.5 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 2 H); ^{13}C NMR δ 10.05, 10.64, 22.75, 43.56, 62.49, 66.22, 137.78, 147.41, 159.49. Anal. Calcd for $C_{12}H_{24}O_3Si_2$: C, 52.89; H, 8.88. Found: C, 53.04; H, 9.17.

(*Z*)-3-[1-(Dimethylphenylsilyl)propylidene]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (2k). IR (neat) 2972, 1432, 1252, 1112, 832 cm^{-1}; ^1H NMR δ 0.05 (s, 3 H), 0.07 (s, 3 H), 0.40 (s, 6 H), 0.90 (t, J = 7.6 Hz, 3 H), 0.94 (t, J = 7.2 Hz, 3 H), 1.38–1.72 (m, 2 H), 2.16–2.40 (m, 3 H), 2.83 (dd, J = 5.5, 16.0 Hz, 1 H), 3.80–3.95 (m, 1 H), 7.28–7.56 (m, 5 H); ^{13}C NMR (C_6D_6) δ -1.39, -1.31, 0.29, 0.58, 9.42, 12.75, 27.55, 30.64, 40.21, 75.46, 127.30, 128.36, 133.82, 138.37, 151.25, 154.09. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.85; H, 9.49. Found: C, 67.65; H, 9.65.

(*Z*)-3-[1-(Dimethylphenylsilyl)propylidene]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (2l). IR (neat) 2968, 1472, 1432, 1252, 1112, 864, 810 cm^{-1}; ^1H NMR δ 0.04 (s, 3 H), 0.05 (s, 3 H), 0.38 (s, 6 H), 0.89 (d, J = 6.4 Hz, 3 H), 0.90 (t, J = 7.4 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H), 1.56–1.78 (m, 1 H), 2.28 (q, J = 7.4 Hz, 2 H), 2.34 (dd, J = 8.4, 16.0 Hz, 1 H), 2.76 (dd, J = 5.8, 16.0 Hz, 1 H), 3.65 (ddd, J = 5.8, 6.8, 8.4 Hz, 1 H), 7.27–7.63 (m, 5 H); ^{13}C NMR δ -0.56, -0.48, 0.96, 1.05, 13.50, 18.06, 18.65, 28.15, 34.49, 37.51, 80.13, 127.69, 128.97, 134.48, 139.20, 152.02, 154.07. Anal. Calcd for $C_{19}H_{32}OSi_2$: C, 68.60; H, 9.70. Found: C, 68.58; H, 9.94.

(*Z*)-3-[1-(Dimethylphenylsilyl)propylidene]-2,2-dimethyl-5-phenyl-1,2-oxasilolane (2m). IR (neat) 2972, 1456, 1432, 1252, 1058, 1032, 864, 808 cm^{-1}; ^1H NMR δ 0.15 (s, 3 H), 0.16 (s, 3 H), 0.42 (s, 3 H), 0.43 (s, 3 H), 0.89 (t, J = 7.6 Hz, 3 H), 2.28 (q, J = 7.6 Hz, 2 H), 2.48 (dd, J = 9.7, 16.0 Hz, 1 H), 3.18 (dd, J = 5.2, 16.0 Hz, 1 H), 4.94 (dd, J = 5.2, 9.7 Hz, 1 H), 7.20–7.6 (m, 10 H); ^{13}C NMR δ -0.70, -0.48,

0.88, 0.99, 13.49, 28.26, 44.07, 76.65, 125.39, 127.15, 127.77, 128.30, 129.09, 134.53, 138.91, 144.72, 152.94, 153.35. Anal. Calcd for $C_{22}H_{30}OSi_2$: C, 72.07; H, 8.25. Found: C, 71.83; H, 8.22.

(Z)-4-Hydroxy-2,2-dimethyl-3-[1-(trimethylsilyl)pentylidene]-1,2-oxasilolane (2n). IR (neat) 3432, 2968, 2880, 1252, 1092, 1064, 952, 858, 828, 788 cm^{-1}; ^1H NMR δ 0.15 (s, 9 H), 0.32 (s, 3 H), 0.41 (s, 3 H), 0.91 (t, J = 7.1 Hz, 3 H), 1.14–1.58 (m, 5 H), 2.22–2.56 (m, 2 H), 3.81 (dd, J = 2.9, 11.0 Hz, 1 H), 4.06 (d, J = 11.0 Hz, 1 H), 4.76 (d, J = 2.9 Hz, 1 H); ^{13}C NMR δ 0.54, 1.18, 1.89, 13.95, 23.14, 33.37, 34.85, 71.82, 72.20, 152.30, 160.00. Anal. Calcd for $C_{13}H_{28}O_2Si_2$: C, 57.29; H, 10.35. Found: C, 57.13; H, 10.60.

(Z)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]perhydro-1,2-oxasilin (2o). IR (neat) 2968, 2928, 1434, 1252, 824 cm^{-1}; ^1H NMR δ 0.11 (s, 9 H), 0.29 (s, 6 H), 1.68–1.81 (m, 2 H), 2.49–2.59 (m, 2 H), 3.92 (t, J = 5.3 Hz, 2 H), 6.19 (t, J = 1.7 Hz, 1 H); ^{13}C NMR δ 0.59, 0.65, 30.69, 44.21, 64.77, 142.35, 159.88. **(*E*)-2,2-Dimethyl-3-[(trimethylsilyl)methylene]perhydro-1,2-oxasilin.** ^1H NMR δ 0.07 (s, 9 H), 0.19 (s, 6 H), 1.73–1.85 (m, 2 H), 2.43–2.51 (m, 2 H), 3.86 (t, J = 5.7 Hz, 2 H), 6.10 (s, 1 H). Anal. Calcd for $C_{10}H_{22}OSi_2$: C, 56.01; H, 10.34. Found: C, 55.80; H, 10.55.

***cis*-3-[(Dimethylphenylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (3b).** Palladium on carbon (5% w/w, 115 mg) was activated by stirring in AcOEt (2 mL) under an atmospheric pressure of hydrogen at room temperature for 10 h, to which **2b** (300 mg, 1.1 mmol) was added. The mixture was stirred at room temperature for 7 h, filtered through Celite, and concentrated to give **3b** (293 mg, 97%) as a mixture of diastereomers. IR (neat) 2968, 1252, 1114, 1030, 982, 832 cm^{-1}; ^1H NMR (major isomer) δ 0.06 (s, 3 H), 0.08 (s, 3 H), 0.31 (s, 6 H), 0.74–1.04 (m, 2 H), 0.95 (d, J = 7.1 Hz, 3 H), 1.10–1.22 (m, 1 H), 2.03–2.23 (m, 1 H), 3.62 (dd, J = 4.1, 9.2 Hz, 1 H), 3.76 (dd, J = 4.6, 9.2 Hz, 1 H), 7.32–7.44 (m, 3 H), 7.46–7.58 (m, 2 H); (minor isomer) δ 3.24 (dd, H-5), 3.97 (dd, H-5);[9] ^{13}C NMR (major isomer) δ -2.82, -2.63, -1.58, -0.26, 10.36, 14.35, 24.17, 38.78, 72.21, 127.76, 128.98, 133.64, 139.14. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.76; H, 9.64.

***cis*-3-[(Dimethylphenylsilyl)methyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (3c).** By a procedure similar to that used to reduce **2b** (room temperature, 5 h), the title compound was obtained from **2c** as a mixture of diastereomers (94%). IR (neat) 2968, 1252, 1114, 830 cm^{-1}; ^1H NMR (major isomer) δ 0.04 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.70–1.90 (m, 9 H), 2.00–2.22 (m, 1 H), 3.60–3.78 (m, 1

H), 7.30–7.66 (m, 5 H); (minor isomer) δ 3.86–4.02 (m, H-5); ^{13}C NMR (major isomer) δ -2.75, -2.65, -2.31, -0.94, 9.85, 16.01, 20.72, 30.56, 42.59, 78.23, 127.73, 128.91, 133.58, 139.29. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.68; H, 9.65. Found: C, 65.57; H, 9.76.

(3*S)-3-[(1*R**)-1-(Dimethylphenylsilyl)ethyl]-2,2-dimethyl-1,2-oxasilolane (3f).** To a mixture of potassium azodicarboxylate (1.40 g, 7.2 mmol) and **2f** (200 mg, 0.72 mmol) in ethanol (4 mL) at 0 °C was added over 20 min AcOH (2.17 g, 36 mmol) in EtOH (1 mL). The mixture was gradually warmed to room temperature overnight with stirring, then diluted with saturated aqueous $NaHCO_3$, and extracted with ether. The organic layer was washed with saturated aqueous $NaHCO_3$, dried over K_2CO_3, and concentrated to afford **3f** (200 mg, 99%). IR (neat) 2968, 2868, 1430, 1252, 1112, 1042, 814 cm^{-1}; ^1H NMR δ 0.15 (s, 3 H), 0.22 (s, 3 H), 0.30 (s, 3 H), 0.33 (s, 3 H), 0.88–1.10 (m, 5 H), 1.34–1.58 (m, 1 H), 1.82–1.96 (m, 1 H), 3.57 (ddd, J = 4.3, 9.3, 11.8 Hz, 1 H), 3.89–4.03 (m, 1 H), 7.32–7.40 (m, 3 H), 7.48–7.59 (m, 2 H); ^{13}C NMR δ -3.74, -3.68, -2.65, 0.63, 17.58, 20.31, 30.47, 33.69, 66.55, 127.68, 128.75, 133.76, 139.32. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.79; H, 9.63.

(3*S,5*S**)-3-[(1*R**)-1-(Dimethylphenylsilyl)propyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (3k).** By a procedure similar to that used to reduce **2f** (-40 °C, 8 h), the title compound was obtained from **2k** as a mixture of diastereomers (97%). IR (neat) 2968, 1252, 1114, 830 cm^{-1}; ^1H NMR (major isomer) δ 0.11 (s, 3 H), 0.24 (s, 3 H), 0.32 (s, 3 H), 0.35 (s, 3 H), 0.72–0.88 (m, 6 H), 0.90–1.65 (m, 7 H), 1.92 (ddd, J = 3.9, 6.8, 12.3 Hz, 1 H), 3.57–3.73 (m, 1 H), 7.28–7.60 (m, 5 H); (minor isomer) δ 3.82–3.98 (m, H-5); ^{13}C NMR (major isomer) δ -2.50, -2.35, -2.13, 0.72, 9.70, 12.87, 26.04, 27.76, 28.62, 30.65, 39.12, 78.53, 127.60, 128.56, 133.64, 140.24. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.41; H, 10.24.

(3*S,5*R**)-3-[(1*R**)-1-(Dimethylphenylsilyl)propyl]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (3l).** By a procedure similar to that used to reduce **2f** (-40 °C, 2 d), the title compound was obtained from **2l** as a mixture of diastereomers (98%). IR (neat) 2968, 1252, 1114, 1044, 834 cm^{-1}; ^1H NMR (major isomer) δ 0.12 (s, 3 H), 0.27 (s, 3 H), 0.34 (s, 3 H), 0.38 (s, 3 H), 0.73 (d, J = 6.7 Hz, 3 H), 0.85 (d, J = 6.2 Hz, 3 H), 0.86 (t, J = 7.2 Hz, 3 H), 0.92–1.68 (m, 6 H), 1.82 (ddd, J = 4.1, 6.9, 12.2 Hz, 1 H), 3.49 (ddd, J = 4.1, 6.1, 10.9 Hz, 1 H), 7.29–7.65 (m, 5 H); (minor isomer) δ 3.62 (ddd, H-5); ^{13}C NMR (major isomer) δ -2.61, -2.45, -2.27, 0.72, 12.88, 17.51, 18.72,

26.04, 27.86, 28.44, 34.25, 36.09, 82.25, 127.60, 128.55, 133.64, 140.24. Anal. Calcd for $C_{19}H_{34}OSi_2$: C, 68.19; H, 10.20. Found: C, 68.15; H, 10.41.

(3*S,5*R**)-3-[(1*R**)-1-(Dimethylphenylsilyl)propyl]-2,2-dimethyl-5-phenyl-1,2-oxasilolane (3m).** By a procedure similar to that used to reduce **2f** (-40 °C, 2 d), the title compound was obtained from **2m** as a mixture of diastereomers (99%). IR (neat) 2968, 1252, 1112, 1046, 864, 838, 700 cm^{-1}; ^1H NMR (major isomer) δ 0.31 (s, 3 H), 0.385 (s, 3 H), 0.391 (s, 3 H), 0.40 (s, 3 H), 0.89 (t, J = 7.4 Hz, 3 H), 1.04–1.29 (m, 1 H), 1.30–1.70 (m, 4 H), 2.33 (ddd, J = 1.6, 4.2, 11.5 Hz, 1 H), 4.84 (dd, J = 4.2, 10.8, 1 H), 7.15–7.64 (m, 10 H); (minor isomer) δ 5.11 (dd, H-5); ^{13}C NMR (major isomer) δ -2.71, -2.05, -1.70, 0.71, 13.04, 26.12, 27.72, 29.67, 42.77, 78.77, 125.19, 126.97, 127.66, 128.17, 128.67, 133.68, 139.73, 144.44. Anal. Calcd for $C_{22}H_{32}OSi_2$: C, 71.68; H, 8.75. Found: C, 71.55; H, 8.71.

3-[1-(Trimethylsilyl)ethyl]-2,2-dimethyl-1,2-oxasilolane (3p and 3p'). The oxasilolane **2p**[3c] was hydrogenated by a procedure similar to that used to reduce **2b**. Filtration through Celite followed by preparative GC afforded a mixture of **3p** and **3p'** (*ca.* 1:1, 33%). ^{13}C NMR δ -2.68, -2.26, -2.02, -1.68, -0.16, 0.69, 14.25, 17.32, 18.58, 20.56, 27.03, 30.55, 31.74, 33.65, 66.26, 66.63.

3-[(Trimethylsilyl)methyl]-2,2-dimethyl-Δ^3-1,2-oxasilolene (5). A mixture of **2a** (100 mg, 0.50 mmol), cyclohexene (3.0 mL) and Pd on carbon (5% w/w, 75 mg) in THF (20 mL) was stirred at 70 °C for 30 h. Filtration through Celite followed by Kugelrohr distillation afforded **5** (84 mg, 84%). IR (neat) 2964, 1252, 1096, 856 cm^{-1}; ^1H NMR δ 0.02 (s, 9 H), 0.22 (s, 6 H), 1.65–1.71 (m, 2 H), 4.52–4.58 (m, 2 H), 6.23–6.28 (m, 1 H); ^{13}C NMR δ -1.27, 0.19, 20.26, 71.76, 137.69, 139.62. Anal. Calcd for $C_9H_{20}OSi_2$: C, 53.93; H, 10.06. Found: C, 53.71; H, 10.09.

(*Z*)-3,4-Bis(dimethylphenylsilyl)-1-phenylhex-3-en-1-ol (6). To a solution of **2m** (106 mg, 0.29 mmol) in ether (0.9 mL) at 0 °C was added PhLi (2.0 M in ether / cyclohexane, 0.43 mmol). The mixture was stirred at 0 °C for 15 min and at room temperature for 3.5 h, diluted with water, and extracted with ether. Evaporation of volatiles afforded **6** (127 mg, 99%). ^1H NMR δ 0.29 (s, 3 H), 0.33 (s, 3 H), 0.47 (s, 6 H), 0.99 (d, J = 7.4 Hz, 3 H), 2.13 (br s, 1 H), 2.21–2.45 (m, 1 H), 2.58–2.80 (m, 1 H), 2.80 (dd, J = 4.1, 13.6 Hz, 1 H), 3.06 (dd, J = 9.6, 13.6 Hz, 1 H), 4.74 (dd, J = 4.1, 9.6 Hz, 1 H), 7.27–7.80 (m, 15 H); ^{13}C NMR δ 0.72, 1.14, 1.61, 1.82, 14.88, 27.51, 43.74, 73.42, 125.50, 127.28, 127.67, 127.81, 128.30, 128.64, 128.81, 133.88, 134.01, 140.37, 140.97, 144.35, 148.04, 160.72.

(2*R,3*S**)-3-Methylbutan-1,2,4-triol Triacetate (7b).** A mixture of **3b** (cis : trans = 89 : 11, 100 mg, 0.36 mmol) and trifluoroacetic acid (818 mg, 7.2 mmol) was stirred at room temperature for 11 h. After removal of trifluoroacetic acid under reduced pressure, KHF_2 (112 mg, 1.4 mmol), MeOH (0.7 mL), KF (42 mg, 0.72 mmol), THF (0.7 mL), H_2O_2 (30% in water, 0.43 mL), and $KHCO_3$ (287 mg, 2.9 mmol) were added to the mixture, which was stirred at room temperature for 29 h. Aqueous $Na_2S_2O_3$ was added and then volatile compounds were thoroughly removed by evaporation. THF (2 mL), Et_3N (545 mg, 5.4 mmol), acetic anhydride (367 mg, 3.59 mmol), and a catalytic amount of 4-(dimethylamino)pyridine were added and the mixture was stirred for 10 h. Column chromatography (hexane : ether = 2 : 1 – 1 : 1) afforded **7b** (84 mg, 95%), whose minor stereoisomer was found to be identical with an authentic sample.[3d] IR (neat) 2984, 1740, 1374, 1232, 1040 cm^{-1}; ^1H NMR δ 0.99 (d, J = 7.0 Hz, 3 H), 2.05 (s, 3 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 2.10–2.30 (m, 1 H), 3.94 (dd, J = 5.9, 11.2 Hz, 1 H), 4.00 (dd, J = 6.9, 11.2 Hz, 1 H), 4.09 (dd, J = 7.2, 11.8 Hz, 1 H), 4.27 (dd, J = 3.9, 11.8 Hz, 1 H), 5.18 (ddd, J = 3.9, 4.6, 7.2 Hz, 1 H); ^{13}C NMR δ 11.71, 20.69, 20.78, 33.77, 63.52, 65.23, 71.15, 170.27, 170.60, 170.84. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.44; H, 7.43.

(3*R,4*S**)-1,3,4-Pentantriol Triacetate (7f).** By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3f** (86%). IR (neat) 2996, 1740, 1438, 1378, 1236, 1052 cm^{-1}; ^1H NMR δ 1.20 (d, J = 6.4 Hz, 3 H), 1.83–1.99 (m, 2 H), 2.03 (s, 6 H), 2.05 (s, 3 H), 3.99–4.20 (m, 2 H), 4.98–5.12 (m, 2 H); ^{13}C NMR δ 15.02, 20.81, 20.85, 21.04, 28.49, 60.41, 70.45, 71.29, 170.23, 170.34, 170.90. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.36; H, 7.52.

(3*S,4*R**,6*R**)-3,4,6-Octantriol Triacetate (7k).** By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3k** (57%). IR (neat) 2980, 2948, 1744, 1374, 1240, 1024 cm^{-1}; ^1H NMR δ 0.85 (t, J = 7.4 Hz, 3 H), 0.87 (t, J = 7.4 Hz, 3 H), 1.47–1.66 (m, 4 H), 1.70–1.92 (m, 2 H), 2.01 (s, 6 H), 2.02 (s, 3 H), 4.74–4.96 (m, 2 H), 4.98–5.12 (m, 1 H); ^{13}C NMR δ 9.24, 9.81, 20.86, 20.93, 21.09, 22.34, 26.27, 32.83, 70.81, 72.29, 75.22, 170.31, 170.49, 170.56. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.35; H, 8.57.

(3*S,5*R**,6*S**)-2-Methyloctan-3,5,6-triol Triacetate (7l).** By a procedure similar to that used to prepare **7b**, the title compound was obtained from **3l** (56%). IR (neat) 2976, 1740, 1468, 1438, 1374, 1240, 1024 cm^{-1}; ^1H NMR δ 0.80–1.05 (m, 9

H), 1.48–1.62 (m, 2 H), 1.75–1.92 (m, 3 H), 2.01 (s, 3 H), 2.03 (s, 6 H), 4.70–4.82 (m, 1 H), 4.83–4.96 (m, 1 H), 5.04 (ddd, J = 3.3, 5.4, 7.4 Hz, 1 H); ^{13}C NMR δ 9.87, 17.09, 18.40, 20.90, 20.96, 21.06, 22.34, 30.74, 71.16, 75.18, 75.23, 170.30, 170.59. Anal. Calcd for $C_{15}H_{26}O_6$: C, 59.58; H, 8.67. Found: C, 59.41; H, 8.96.

(1*S,3*R**,4*S**)-1-Phenylhexan-1,3,4-triol Triacetate (7m).** A mixture of **3m** (100 mg, 0.27 mmol) and potassium *t*-butoxide (32 mg, 0.29 mmol) in DMSO (1 mL) was stirred at room temperature for 1 h. The mixture was diluted with phosphate buffer solution (pH 7), extracted with ether, washed with water, dried over Na_2SO_4, and evaporated. To the residual oil were added tetrabutylammonium fluoride (1 M in THF, 1.1 mL, 1.1 mmol), MeOH (1 mL), H_2O_2 (30% in water, 0.33 mL) and $KHCO_3$ (54 mg, 0.54 mmol), and the mixture was stirred at 40 °C for 12 h. Aqueous $Na_2S_2O_3$ was added and then volatile compounds were thoroughly removed by evaporation. The residue was acetylated by a procedure similar to that used for **7b** to give **7m** (71 mg, 78%). IR (neat) 2984, 1740, 1374, 1248, 1024 cm^{-1}; ^{1}H NMR δ 0.82 (t, J = 7.4 Hz, 3 H), 1.40–1.53 (m, 2 H), 1.98 (s, 3 H), 2.00–2.15 (m, 1 H), 2.06 (s, 3 H), 2.07 (s, 3 H), 2.29 (ddd, J = 5.9, 9.5, 14.4 Hz, 1 H), 4.80 (dt, J = 9.5, 3.1 Hz, 1 H), 4.93 (ddd, J = 3.1, 5.2, 8.3 Hz, 1 H), 5.78 (dd, J = 5.9, 8.1 Hz, 1 H), 7.25–7.40 (m, 5 H); ^{13}C NMR δ 9.72, 20.85, 20.90, 21.17, 22.83, 35.23, 70.84, 73.24, 74.96, 126.55, 128.31, 128.63, 139.23, 169.92, 170.17, 170.54. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 63.99; H, 7.30.

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(5) The *syn* addition of the Si–Si linkages in the produced 1,2-oxasilolanes **2a–c,e,f,m,o** was deduced from NOE experiments. The stereochemistry of the other bis-silylated products **2** was assigned by analogy.

(6) The stereochemical assignment of **3b** was based on the oxidative transformation to **7b**. The relationship between the 3- and 5-substituents of **3c,k–m** was elucidated according to the ^{1}H NMR chemical shift correlation method.[9]

(7) High degrees of regio- and stereospecificities have been observed in numerous examples of diimide reductions of C–C double bonds. This advantage of diimide reduction has been utilized to determine the positions of unsaturation in naturally derived fatty acids; Pasto, D. J.; Tailor, R. T. In *Organic Reactions*, Vol. 40; Paquette, L. A., Ed.; John Wiley and Sons Inc.; 1991, pp. 91–155, and references cited therein. The stereochemical assignment of the side chains of **3f,k–m** is based on the assumption that the direct *syn* addition of hydrogen to the C–C double bonds took place.

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(9) When **3m** was treated with trifluoroacetic acid, intramolecular migration of the phenyl group from the silicon to the benzylic carbon took place giving 1,1-diphenylhexan-3,4-diol after oxidation.

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Chapter 2

Reactions of Si–Si σ-Bonds with Bis(*t*-alkyl isocyanide)palladium(0) Complexes. Synthesis and Reactions of Cyclic Bis(organosilyl)palladium Complexes

Abstract: Four- to seven-membered cyclic bis(organosilyl)palladium(II) complexes were synthesized by oxidative addition of cyclic disilanes onto bis(*t*-butyl isocyanide)palladium(0) as well as by intramolecular metathesis of the two Si–Si bonds of bis(disilane)s with the palladium(0) complex. The 4-membered bis(organosilyl)bis(*t*-butyl isocyanide)palladium complex prepared from 2,2-bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane was characterized by a single-crystal X-ray method, which showed an unusually short cross-ring Si–Si distance in the 4-membered ring. The reactivities of the cyclic bis(organosilyl)bis(*t*-butyl isocyanide)palladium complexes toward phosphines, cyclic disilanes, and alkynes were also examined. Cyclic organosilicon compounds were synthesized by bis-silylation of alkynes with cyclic bis(organosilyl)palladium intermediates generated by the intramolecular metathesis. The bis-silylation was also applicable for electron-deficient alkenes: α,β-unsaturated ketones gave 7-membered 1,4-bis-silylation adducts, whereas the corresponding ester and nitrile gave 5-membered 1,2-adducts in high yields.

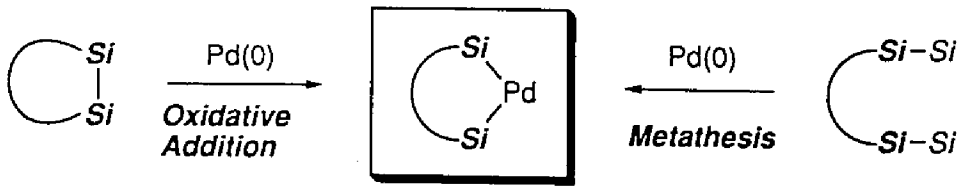
Introduction

The intriguing chemical and physical properties of the Si–Si σ-bond are due to its high-lying HOMO and low-lying LUMO, which should be compared with those of a carbon-carbon double bond. The MO interaction with low valent transition metal complexes has made possible some synthetic uses of disilanes. Especially, palladium-catalyzed bis-silylation of unsaturated organic compounds,[1] e.g., alkynes,[2,3] alkenes,[2l,4,5] dienes,[2g,h,j,k,6] isocyanides,[7] and α,β-unsaturated ketones[8] provided a convenient method for formation of carbon–silicon bonds. The reactions commonly involve an oxidative addition of the Si–Si bond onto palladium, which is crucially important in the catalytic cycles. The relevant interaction of the Si–Si σ-bond with palladium complexes could lead to metathesis, i.e., disproportionation reaction of the Si–Si σ-bond.[2c,9–11] Cyclooligomerization of cyclic disilanes through Si–Si σ-bond metathesis has been reported, though the mechanistic details still remain to be understood.[2c,10,11]

Recently, generation and isolation, as well as synthetic application of bis(organosilyl)palladium complexes, have been reported by some research groups.[2l,12–14] Ito and co-workers have also found a new catalytic system, *t*-alkyl isocyanide–$Pd(OAc)_2$, for use as a highly active catalyst for bis-silylations of alkynes and alkenes.[3,4,15] The synthetic usefulness of intramolecular bis-silylation of alkenes has been demonstrated by stereoselective synthesis of polyols.

In such catalysis, they presumed that bis(*t*-alkyl isocyanide)palladium(0) complexes might be responsible for the primary active species, onto which Si–Si bond would undergo oxidative addition to form bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) complexes. In this chapter, the author describes the palladium-catalyzed bis-silylation, focusing on preparation and reactions of cyclic bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) complexes (Scheme 1).[16]

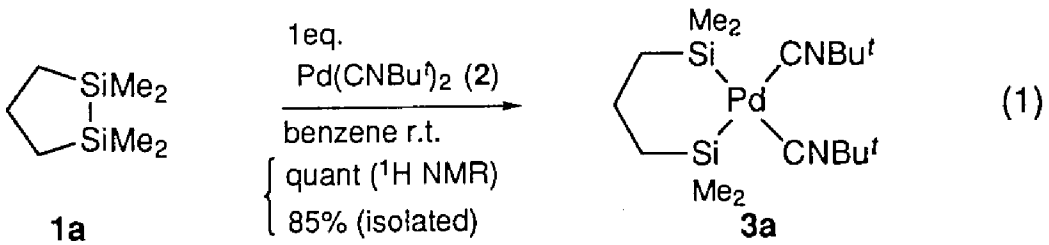
Scheme 1.



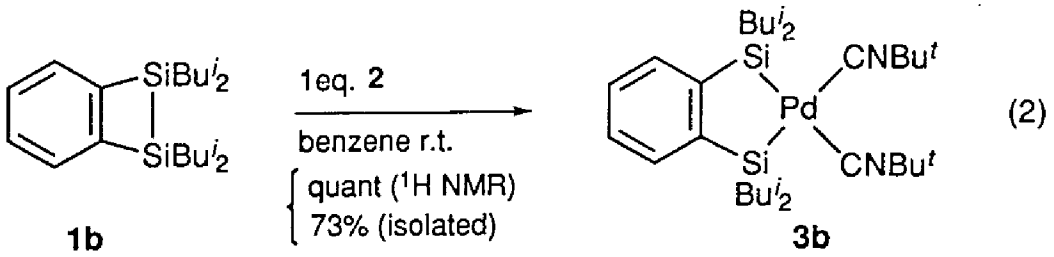
Results and Discussion

Generation of Cyclic Bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) Complexes: Oxidative Addition of Si–Si Bonds onto Bis(*t*-alkyl isocyanide)palladium(0). It has been well documented that disilanes bearing electronegative substituents on silicon atoms as well as strained cyclic disilanes may readily undergo oxidative addition onto palladium(0). Though synthesis of bis(organosilyl)palladium complexes has been achieved by use of hydrodisilanes[13] as well as fluorodisilanes[21] with low valent phosphine-palladium complexes,[17] isolation and characterization of the cyclic transition metal complexes from cyclic disilanes have never been reported.[18,19]

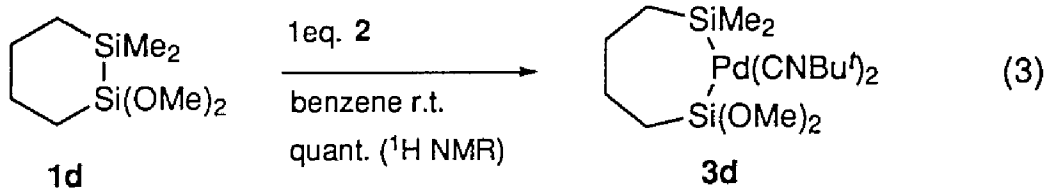
1,1,2,2-Tetramethyl-1,2-disilacyclopentane (**1a**), which has been known as a strained, reactive cyclic disilane, was reacted with bis(*t*-butyl isocyanide)palladium(0) (**2**) at room temperature in benzene. Monitoring of the reaction by ^{1}H NMR spectroscopy revealed a rapid conversion (5 minutes) to 6-membered bis(organosilyl)palladium complex **3a** (eq 1). The complex was isolated in 85% yield as colorless crystals. In this reaction, *t*-butyl isocyanide was a ligand of choice on palladium(0). Use of tetrakis(triphenylphosphine)palladium(0) did not give any complexes corresponding to **3a** in the reaction with **1a**, even at high temperature. The much-strained 4-membered cyclic disilane **1b** also gave the corresponding 5-membered bis(organosilyl)palladium complex **3b** in high yield (eq 2). But, 1,1,2,2-tetramethyl-1,2-disilacyclohexane (**1c**) did not react at all under the same reaction conditions, presumably because of the lack of ring strain. However, substitution of the two methyl groups on the silicon atom (in **1c**) by two methoxy groups (in **1d**) resulted in clean formation of 7-membered bis(organosilyl)palladium complex **3d** (eq 3).



(1)

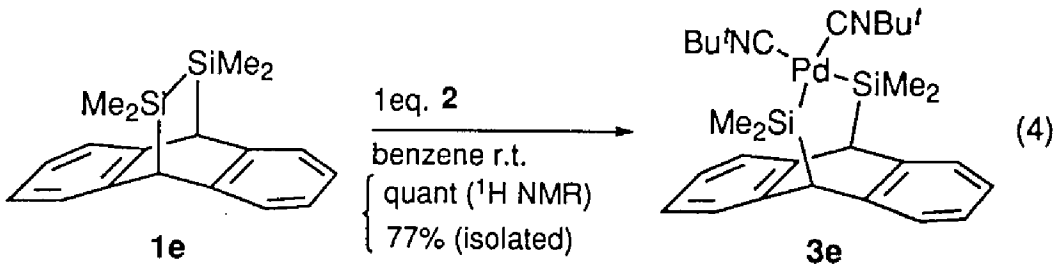


1b **3b** (2)



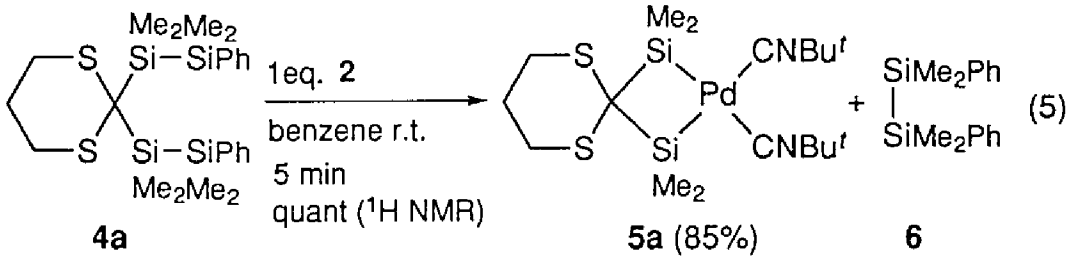
1d **3d** (3)

Bicyclic disilane **1e** was also reactive toward **2**, producing the corresponding bis(organosilyl)palladium complex 3e in nearly quantitative yield (eq 4).



1e **3e** (4)

Generation of Cyclic Bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) Complexes: Intramolecular Metathesis of Si–Si Bonds onto Bis(*t*-alkyl isocyanide)palladium(0). Bis(*t*-butyl isocyanide)palladium(0) (**2**) also mediated simultaneous activation of two Si–Si bonds oriented appropriately in a molecule. Thus, the reaction of bis(disilanyl)dithiane **4a** with **2** was monitored by ^{1}H NMR, resulting in quantitative formation of 4-membered cyclic bis(organosilyl)palladium complex **5a** and *sym*-tetramethyldiphenyldisilane (**6**) (eq 5). The metathesis reaction completed within 5 minutes to afford **5a**, which was isolated as a crystalline solid in high yield on addition of pentane to the reaction mixture. It is noted that tetrakis(triphenylphosphine)palladium(0) failed to afford the complex corresponding to **5a**. The structure of **5a** was established by a single-crystal X-ray diffraction study. The crystal structure is shown in Figure 1, together with selected bond distances and angles. The two silicon, two isocyano carbon, and palladium atoms are nearly on the same plane. The two isocyanide ligands coordinate to palladium with a relatively large angle (C–Pd–C = 105.9(2)°). The unusual short cross-ring Si–Si distance (2.613(2) Å) may suggest a possibility of covalently bonded Si–Si in the 4-membered ring.[20,21]



4a **5a** (85%) **6**

Reactions of some other bis(disilanyl)alkanes with **2** were examined. The success of the intramolecular metathesis depended on the tethers connecting the two disilanyl groups (Scheme 2). Bis(disilanyl)methane **4b** conceivably underwent the intramolecular metathesis to give *sym*-tetramethyldiphenyldisilane, although the expected 4-membered bis(organosilyl)palladium complex **5b** could not be detected by ^{1}H NMR spectroscopy. 1,2-Bis(disilanyl)ethane **4c** and 1,3-bis(disilanyl)propane **4d** gave the corresponding cyclic bis(organosilyl)palladium complex **5c** and **3a**, respectively, the reaction of the latter being much slower. No reaction took place with 1,4-bis(disilanyl)butane **4e**, which had a longer tether.

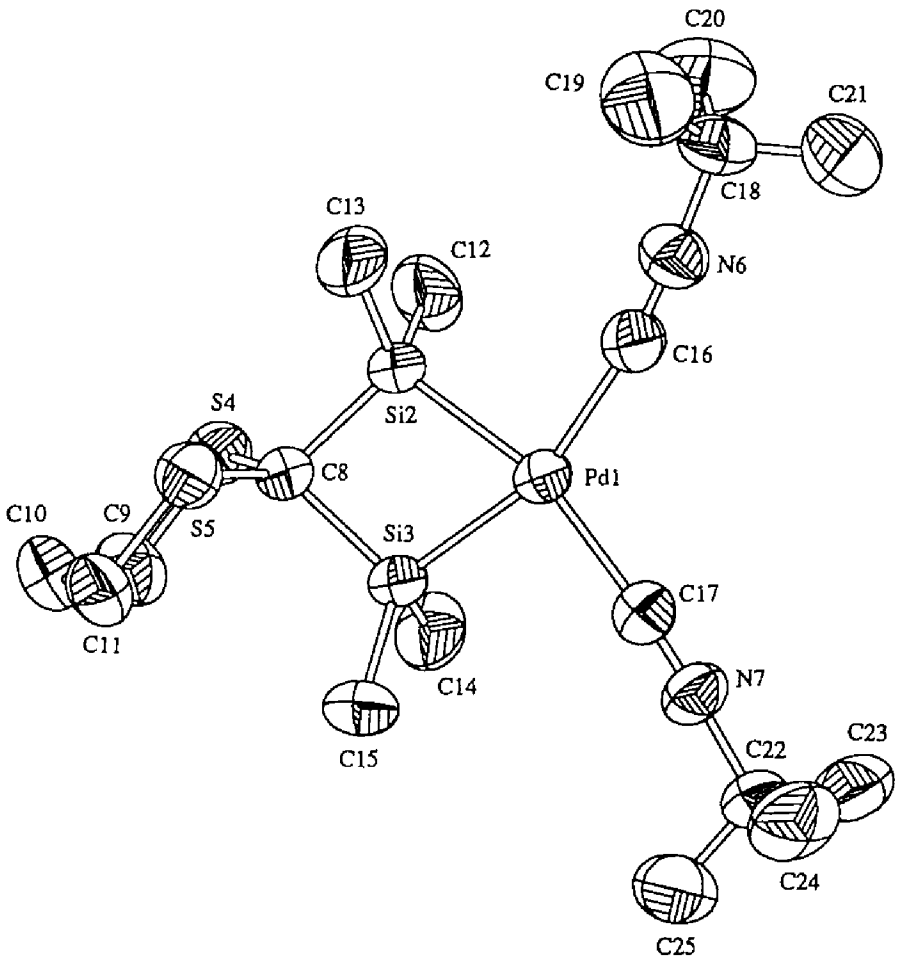
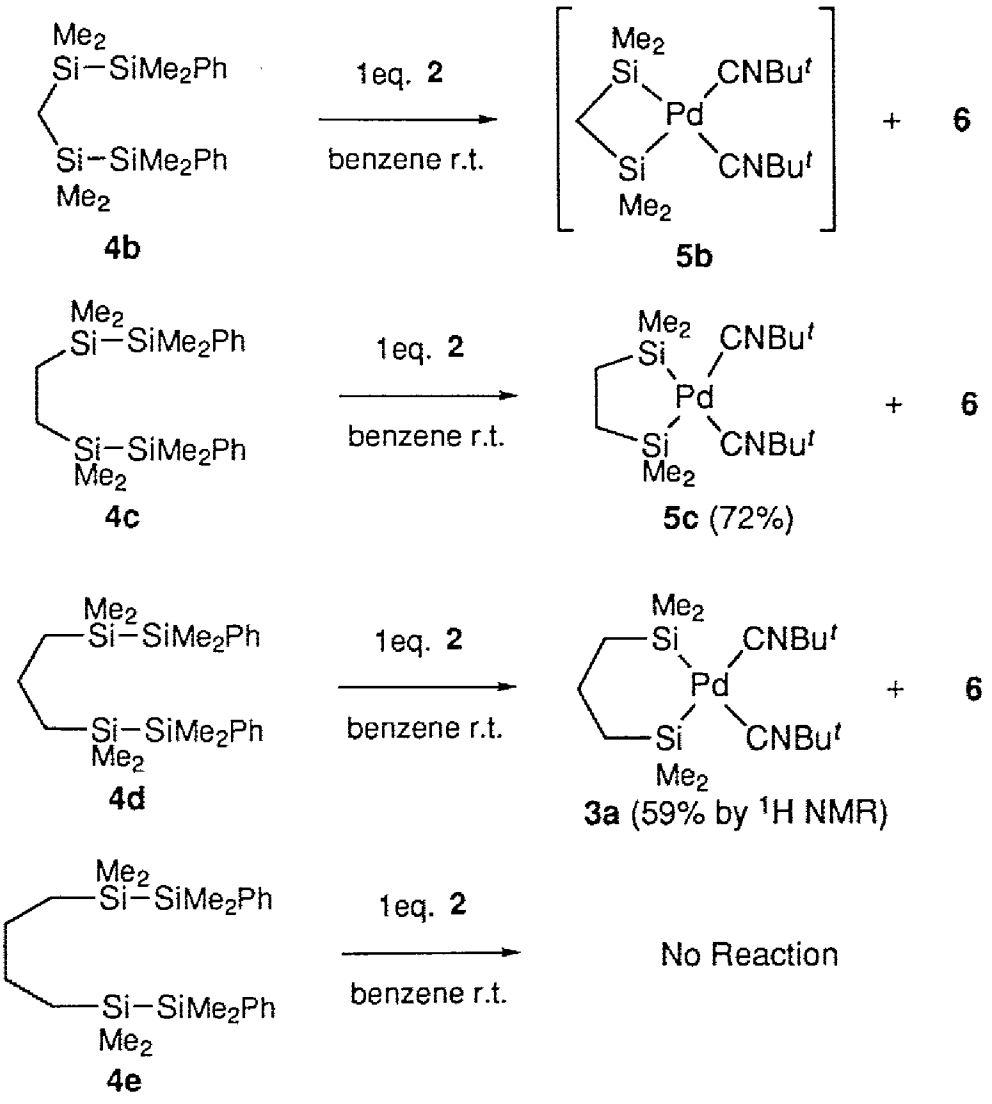


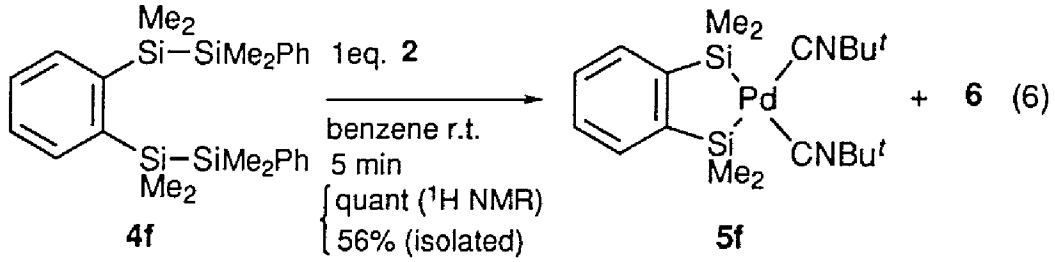
Figure 1. Crystal structure of **5a**. The thermal elipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)–Si(2) = 2.336 (1), Pd(1)–Si(3) = 2.356 (1), Pd(1)–C(16) = 2.053 (5), Pd(1)–C(17) = 2.053 (4), Si(2)–Si(3) = 2.613 (2), N(6)–C(16) = 1.151 (6), N(7)–C(17) = 1.146 (6); Si(2)–Pd(1)–Si(3) = 67.68 (4), Si(2)–Pd(1)–C(16) = 92.0 (1), C(16)–Pd(1)–C(17) = 105.9 (2), Si(3)–Pd(1)–C(17) = 94.4 (1), Pd(1)–Si(2)–C(8) = 103.0 (1), Pd(1)–Si(3)–C(8) = 102.3 (1), Si(2)–C(8)–Si(3) = 85.1 (1), Pd(1)–C(16)–N(6) = 171.3 (4), Pd(1)–C(17)–N(7) = 173.8 (4), C(16)–N(6)–C(18) = 175.8 (4), C(17)–N(7)–C(22) = 177.5 (4).

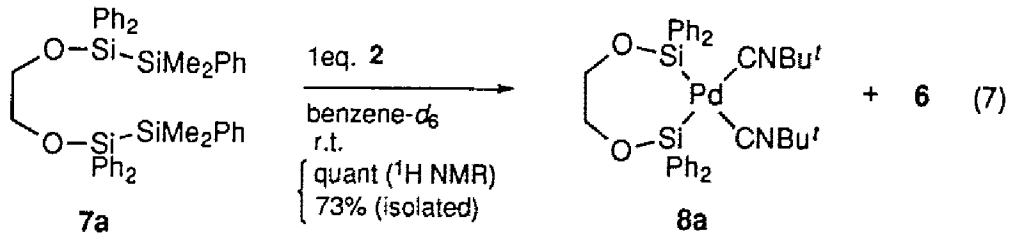
Scheme 2.



o-Bis(disilanyl)benzene **4f** also underwent the intramolecular metathesis very rapidly to give **5f** in high yield (eq 6). Ethylene glycol derived bis(disilanyl ether) **7a** underwent intramolecular metathesis to give 7-membered bis(organosilyl)palladium complex **8a** in good yield (eq 7). This may suggest, by comparison with results for **4e**, that the oxygen substituent and phenyl groups on the silicon atom favor the in-

tramolecular metathesis. Accordingly, reaction of tartrate-derived **7b** proceeded smoothly to give **8b** in high yield (eq 8). Similarly, bis(disilanyl ether)s with longer tethers (**7c, d**) gave the corresponding cyclic complexes and *sym*-tetramethyldiphenyldisilane (**6**), although the reactions were too sluggish to obtain the complexes in reasonable yields (Chart 1).





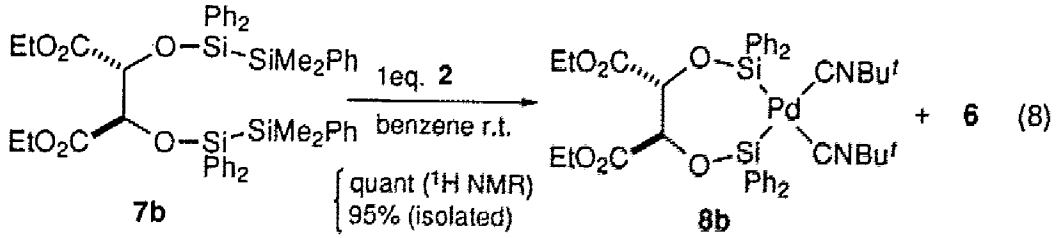
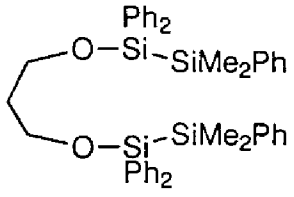
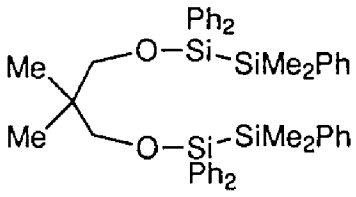


Chart 1.



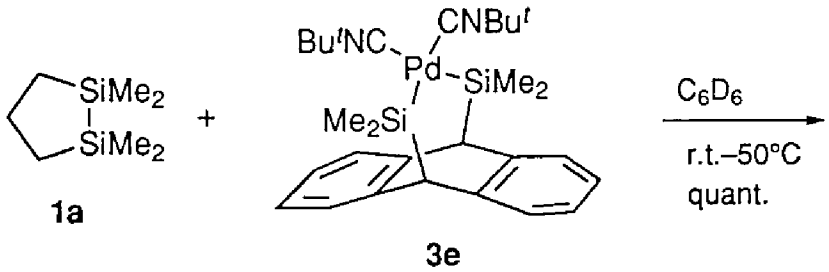
7c



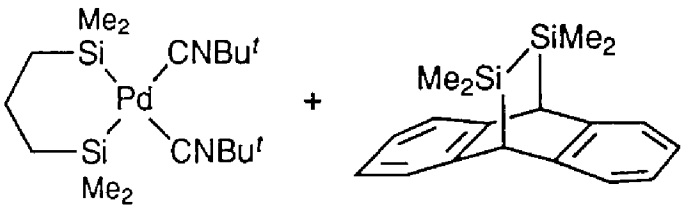
7d

Reactions of Cyclic Bis(organosilyl)palladium Complexes *with Disilanes.* Reversibility of the oxidative addition of the Si–Si bonds onto palladium(0) was confirmed by exchange reaction with disilane in benzene-d_6. Addition of 1 equivalent of 5-membered disilane **1a** to bis(organosilyl)palladium complex **3e** afforded 6-membered **3a** and disilane **1e** in quantitative yield, as indicated by ^{1}H NMR (Scheme 3).

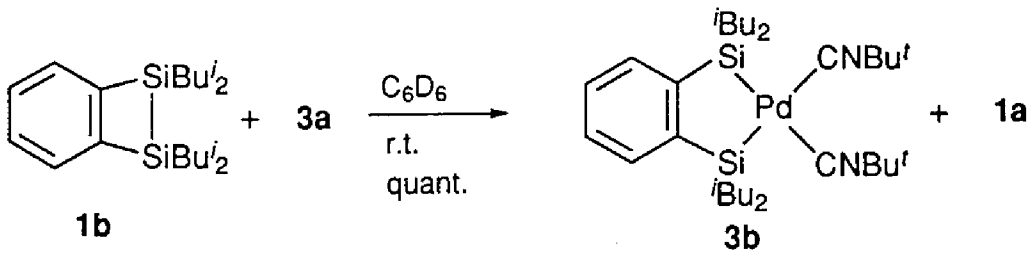
Scheme 3.



1a **3e**

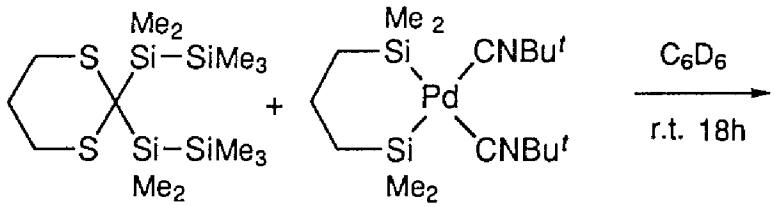


3a **1e**

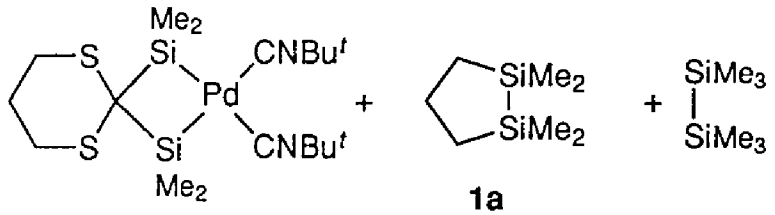


1b **3b**

Moreover, when 4-membered disilane **1b** was added to **3a** in benzene-d_6, disilane exchange reaction occurred rapidly to give 5-membered complex **3b** along with dissociated **1a**. These results indicate that the disilane exchange proceeded via reversible oxidative addition/reductive elimination process with predominant dissociation of less-strained cyclic disilanes. The reversibility was also evidenced by reaction of **3a** with bis(disilanyl)dithiane **4g**, giving **5a** via intramolecular metathesis reaction (eq 9).



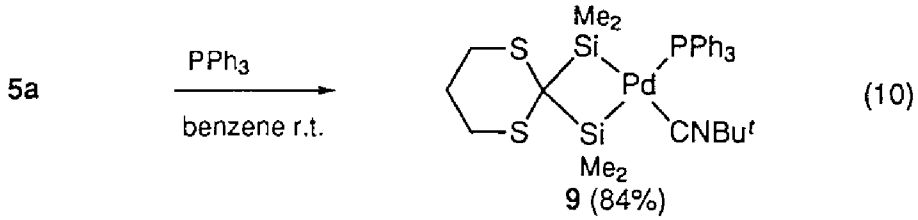
4g **3a** (9)



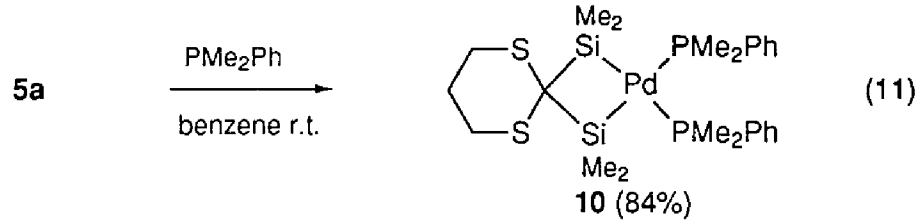
5a 75% (^{1}H NMR) **1a**

With Phosphines. One of the two *t*-butyl isocyanide ligands of the complex **5a** was selectively replaced by PPh_3 to give bis(organosilyl)complex **9**, having both isocyanide and phosphine as ligands (eq 10). Presumably, steric congestion on the palladium disfavored further ligand exchange. In contrast, Me_2PhP replaced the two isocyanides to give bis(organosilyl)bis(phosphine)palladium complex **10** in good yield, this complex has not been otherwise accessible (eq 11).

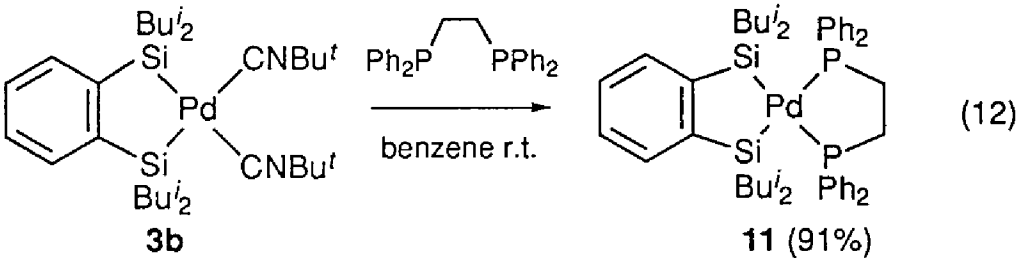
Similarly, bis(organosilyl)(dppe)palladium complexes **11** was synthesized by replacement of the two isocyanides of **3b** with bis(diphenylphosphino)ethane (dppe) (eq 12). The structure of **11** was confirmed by a single-crystal X-ray analysis (Figure 2).



(10)



(11)



(12)

Unlike 4- and 5-membered bis(organosilyl)bis(*t*-butyl isocyanide)palladium complexes, addition of bis(diphenylphosphino)ethane to a benzene-d_6 solution of 6-membered complex **3a** resulted in reductive elimination of disilane **1a** (45% by ^{1}H NMR) with an unidentified palladium complex having a dppe ligand.

Catalytic Bis-Silylation of Alkynes and Alkenes via Intramolecular Metathesis of Si–Si Bonds. A stoichiometric reaction of 4-membered bis(organosilyl)palladium(II) complex **5a** with terminal and internal alkynes took place smoothly at room temperature, giving the corresponding spiro-disilacyclopentene derivatives in high yields, except for the reaction with diphenylacetylene, which was carried out in toluene at 90°C (Table 1). However, the bis-silylation reactions with dialkylacetylenes have all failed.

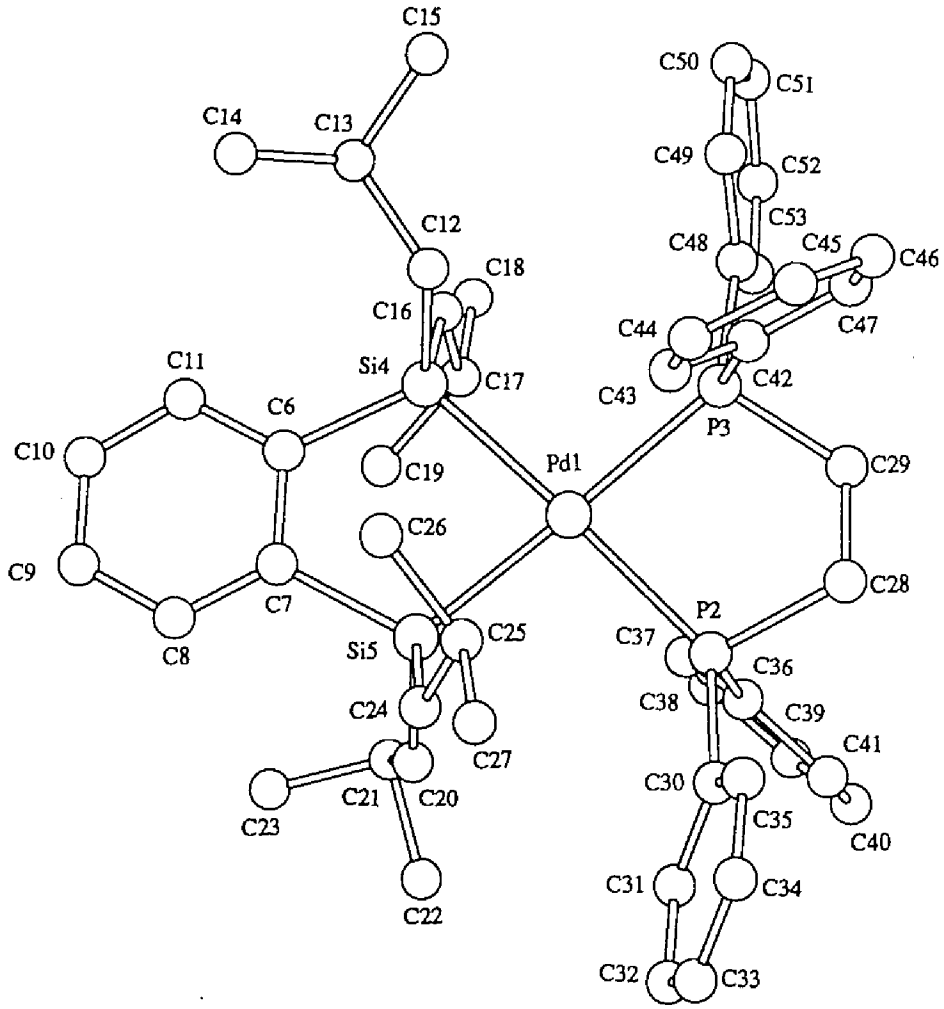
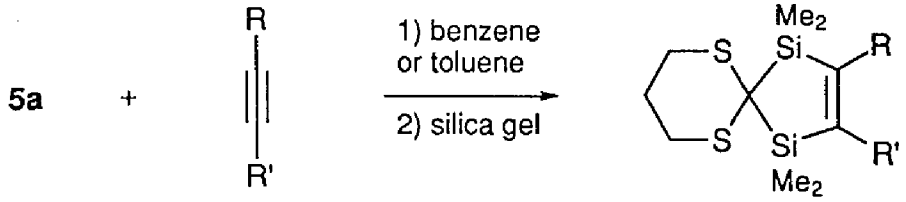


Figure 2. Crystal structure of **11**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)–Si(4) = 2.375 (4), Pd(1)–Si(5) = 2.368 (4), Pd(1)–P(2) = 2.365 (4), Pd(1)–P(3) = 2.364 (4); Si(4)–Pd(1)–Si(5) = 80.9 (2), P(2)–Pd(1)–Si(5) = 98.0 (2), P(3)–Pd(1)–Si(4) = 98.6 (2), P(2)–Pd(1)–P(3) = 83.9 (2), Pd(1)–Si(4)–C(6) = 113.1 (5), Pd(1)–Si(5)–C(7) = 113.6 (5), Si(4)–C(6)–C(7) = 116.8 (10), Si(5)–C(7)–C(6) = 115.0 (10).

Table 1. Stoichiometric Reaction of **5a** with Alkynes



entry	alkyne	conditions	products (yield / %)
1	Ph—≡—H	benzene, r.t., 5 min	**12a** (98)
2	Me_3Si—≡—H	toluene, r.t., 3.5 h	**13** (90)
3	MeO_2C—≡—CO_2Me	benzene, r.t., 5 min	**14** (99)
4	Ph—≡—Ph	toluene, 90°C, 12 h	**15** (96)

Bis(disilanyl)alkanes were subjected to the reaction with phenylacetylene in the presence of a catalytic amount of palladium–isonitrile catalyst, which was generated in-situ from $Pd(OAc)_2$ and 1,1,3,3-tetramethylbutyl isocyanide (eq 13: Table 2). The reaction with bis(disilanyl)methane **4b** afforded 5-membered cyclic product **12b** only in low yield together with acyclic products **16b** and **17b** (76% in total, entry 1).

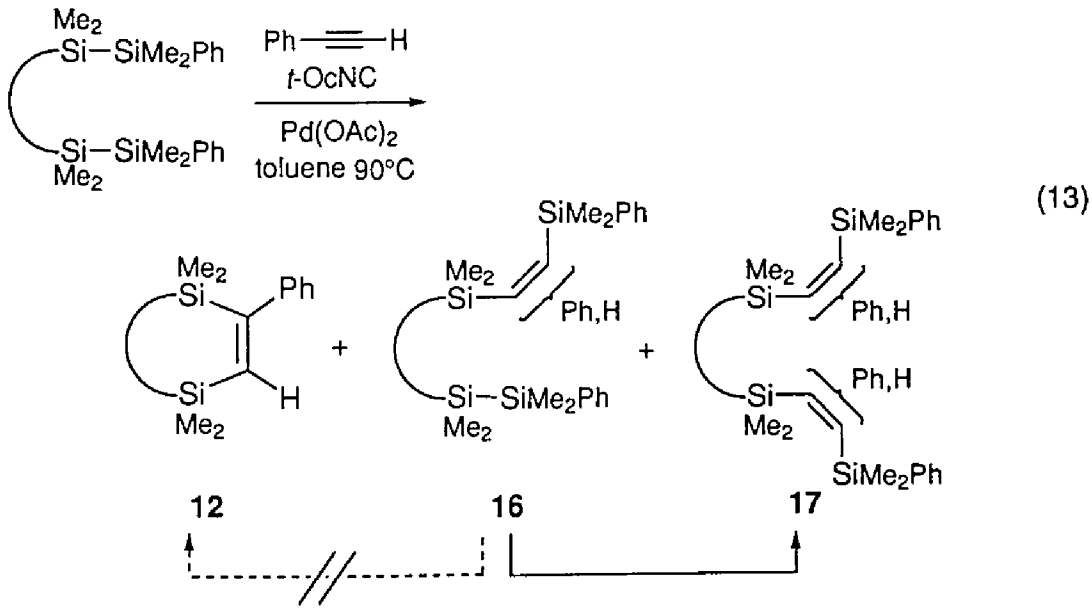
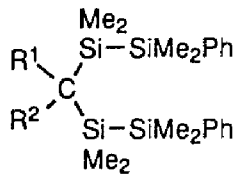


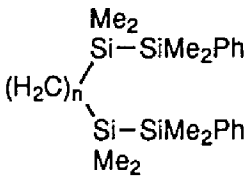
Table 2. Palladium-Catalyzed Reaction of Bis(disilanyl)alkanes[a] with Phenylacetylene at 90°C[b]

entry	substrate (4)	**12** (%yield)[c]	**16**	**17** (%yield)[c]
1	**b**	4	48	28
2[d]	**h**	67	18	<3
3	**i**	91	0	0
4	**j**	97	0	0
5	**a**	91	0	0
6	**c**	39	15	30
7	**d**	0	50	33
8	**e**	0	38	49

[a] List of bis(disilanyl)alkanes used in the reaction:



4b (R^1=R^2=H)
h (R^1=Me, R^2=H)
I (R^1=OPh, R^2=H)
J (R^1=SPh, R^2=H)
a (R^1,R^2=$S(CH_2)_3S$)

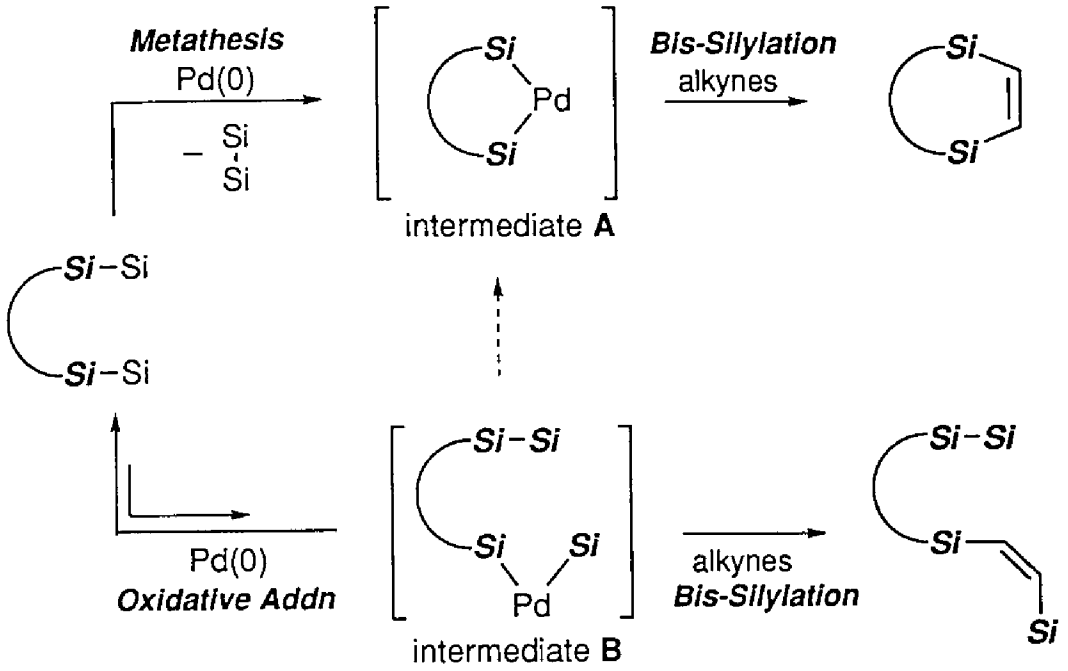


4c (n = 2)
d (n = 3)
e (n = 4)

[b] All reactions used $Pd(OAc)_2$ (0.02 eq.), 1,1,3,3-tetrametylbutyl isocyanide (0.3 eq.), and phenylacetylene (3 eq.) unless otherwise noted. [c] Isolated yield.
[d] $Pd(OAc)_2$ (0.1 eq.), 1,1,3,3-tetrametylbutyl isocyanide (1.5 eq.) were used.

The formation of **12b** may suggest that a cyclic bis(organosilyl)palladium(II) intermediate **A** is generated by concerted metathesis or stepwise metathesis via intermediate **B**, which undergoes a bis-silylation reaction with phenylacetylene. On the other hand, bis-silylation with intermediate **B** may lead to the formation of acyclic **16b** and **17b** (Scheme 4).

Scheme 4.

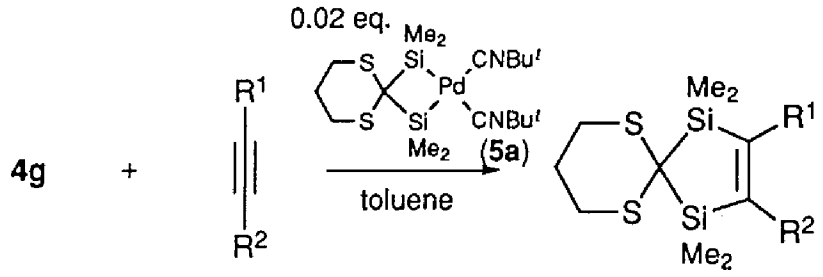


As shown in Table 2, introduction of substituents at the methylene tether of **4b** favored the formation of the cyclic intermediate **A** through the Si–Si metathesis, i.e., methyl substituted **4h** gave **12h** in 67% yield (entry 2). Selective bis-silylation of phenyacetylene with intermediate **A** was carried out in the reactions of phenoxy-substituted **4i**, phenylthio-substituted **4j** and trimethylenedithio-substituted **4a** to provide exclusively the corresponding 5-membered cyclic products **12i**, **12j**, and **12a**, respectively, in high yields (entries 3–5).

On the other hand, bis(disilanyl)alkanes **4c, 4d,** and **4e** tethered by C_2, C_3, and C_4 chains preferred the bis-silylation with phenylacetylene via intermediate **B** (entries 6–8), although 1,2-bis(disilanyl)ethane **4c** competitively underwent the reaction via intermediate **A**, leading to the 6-membered 1-phenyl-3,6-disila-1-cyclohexene **12c** (39%). As expected, the bis-silylation product **16c** once formed was reacted with phenylacetylene under the same reaction conditions to afford selectively acyclic diene **17c**.

The catalytic bis-silylation with **4g** also proceeded in the presence of a catalytic amount of isolated **5a** without an excess of *t*-butyl isocyanide (Table 3).[3,4] Not only terminal alkynes, but also conjugated ynone furnished the respective bis-silylation products in moderate to high yields. Internal alkyne, however, provided the corresponding products **15** only in low yield.

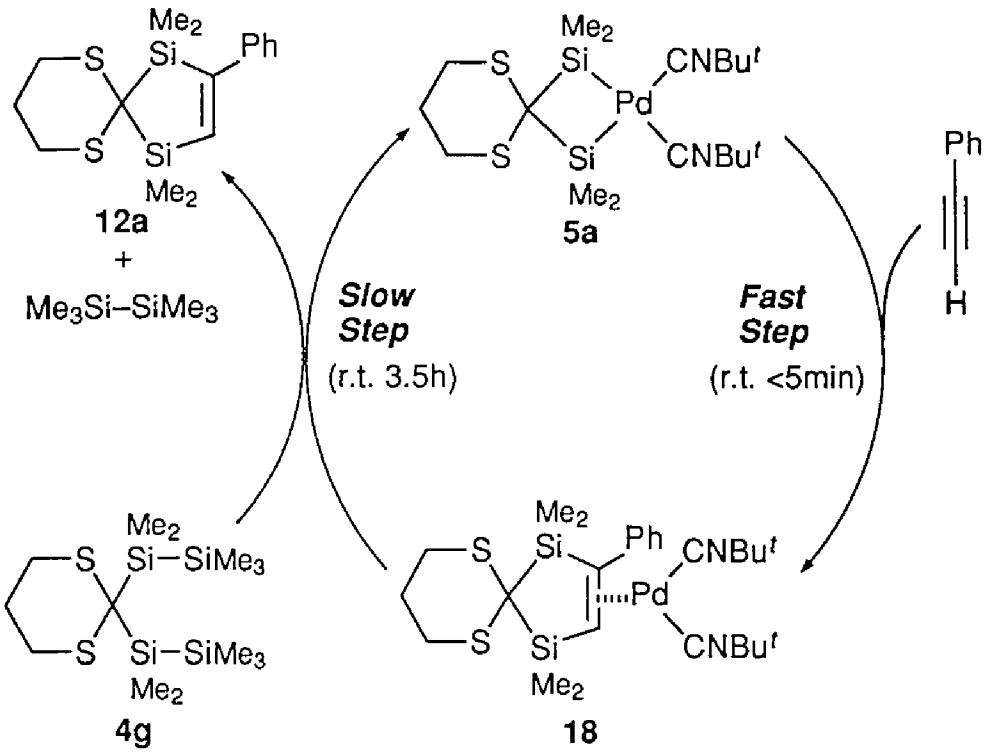
Table 3. Catalytic Bis-Silylation of Alkynes in the presence of **5a**



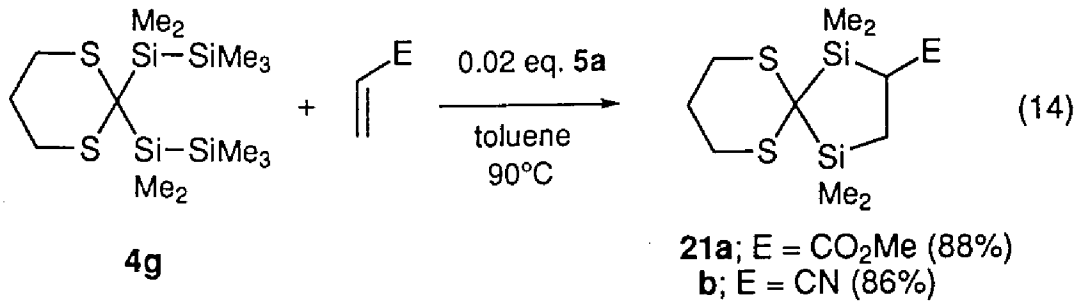
entry	alkyne	conditions	products (yield / %)
1	Ph—≡—H	80°C, 2h	**12a** (93)
2	Me_3Si—≡—H	110°C, 12h	**13** (96)
3	*n*-Hex—≡—H	110°C, 1h	**19** (97)
4	*n*-Bu—≡—COMe	90°C, 11h	**20** (78)
5	Ph—≡—Ph	110°C, 67h	**15** (13)

^{1}H NMR study of the stoichiometric bis-silylation of phenylacetylene with **5a** revealed a rapid formation of bis(*t*-butyl isocyanide)(spiro-disilacyclopentene)palladium(0) **18**, which is spectroscopically identified by comparison with the palladium complex formed in the reaction of **12a** with bis(*t*-butyl isocyanide)palladium(0) (**2**). It is notable that the oxidative metathesis of **4g** onto **18** is involved as a rate determining step, regenerating **5a** with **12a** (Scheme 5).

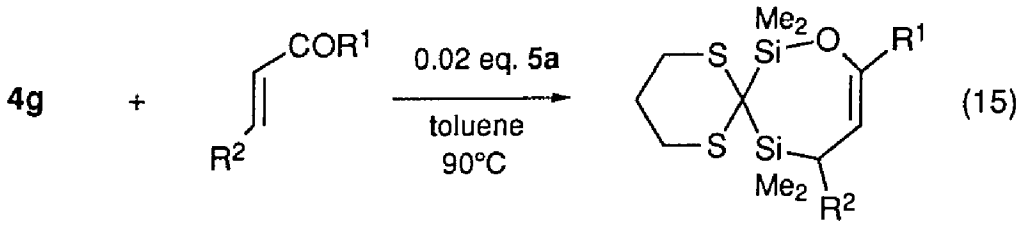
Scheme 5.



Furthermore, the catalytic bis-silylation with bis(disilanyl)dithiane **4g** was successfully applied to some electron-deficient olefins. α,β-Unsaturated ester and nitrile provided 1,2-bis-silylation adducts **21** (eq 14), whereas the corresponding ketones gave 1,4-adducts **22** (eq 15).[22] It may be remarked that no products derived from insertion of the alkenes into the Si–Si bonds of the starting **4g** and hexamethyldisilane produced in the reaction were detectable. This indicates the intramolecular metathesis of the Si–Si σ-bonds of **4g** by bis(*t*-butyl isocyanide)palladium(0) was a highly favorable process giving reactive, cyclic bis(organosilyl)palladium complexes.



(14)



(15)

22a; R^1=Me, R^2=H (96%)
b; R^1=R^2=Me (99%)
c; R^1=Ph, R^2=H (82%)

Conclusion

The author found that 4- to 7-membered cyclic bis(organosilyl)bis(*t*-butyl isocyanide)palladium(II) complexes were formed by the reaction of bis(*t*-butyl isocyanide)palladium(0) with cyclic disilanes or acyclic bis(disilane)s. Especially, intramolecular metathesis of bis(disilanyl)methane derivatives made possible the synthesis of 4-membered bis(organosilyl)palladium complexes, which were otherwise difficult to synthesize. New synthetic access to cyclic organosilicon compounds was demonstrated by bis-silylation of alkynes and alkenes with the cyclic bis(organosilyl)palladium complex.

Experimental Section

General. All reactions were carried out under a dry nitrogen or an argon atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Varian VXR-200. Proton chemical shifts are referenced to internal residual solvent protons: $CDCl_3$, 7.25; C_6D_6, 7.20; CD_2Cl_2, 5.35. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents: $CDCl_3$, 77.0; C_6D_6, 128.0; CD_2Cl_2, 53.8. Silicon and phosphorous chemical shifts are referenced to the signals of tetramethylsilane and phosphoric acid (85%), respectively. Melting point were uncorrected. IR spectra were recorded with a Hitachi 270-30 spectrometer. Electron impact mass spectra (MS) were recorded with a JEOL LMS-D300 spectrometer.

Starting Materials. Compounds **1a**,[23] **b**,[24] **c**,[23] **e**,[25] and **4c**,[26] were prepared by the methods reported in the literature. Compound **1d** was prepared from 2,2-dimethyl-1,1-diphenyl-1,2-disilacyclohexane by the reaction with HCl gas in the presence of a catalytic amount of $AlCl_3$ followed by treatment with methanol in the presence of triethylamine. Compound **4b** was prepared from **4a** by reduction with Ca in liquid ammonia.[27] Compound **4d** was prepared by the reaction of dimethylphenylsilyllithium with 3-(chlorodimethylsilyl)-1-(1,1,2,2-tetramethyl-2-phenyldisilanyl)propane, which was synthesized by platinum-catalyzed hydrosilylation of 3-(1,1,2,2-tetramethyl-2-phenyldisilanyl)propene with chlorodimethylsilane. Compound **4e** was prepared by the reaction of 1-chloro-1,1,2,2-tetramethy-2-phenyldisilane with 1,4-butanediylbis(magnesium bromide). Compound **4f** was prepared by the reaction of dimethylphenylsilyllithium with 1,2-bis(chlorodimethylsilyl)benzene.[28] Compounds **7a** and **7b** were prepared from the corresponding alcohols and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane in the presence of triethylamine. Compound **4h** was prepared from **4j** by the reaction with lithium naphthalenide followed by treatment with iodomethane.[29] Procedures for preparation of **2**, **4a**, **4g**, **4i**, and **4j** are described below.

Preparation of Bis(*t*-butyl isocyanide)palladium(0) (2). The procedure reported by Otsuka et.al.[30] was followed with slight modification. To a pentane solution of $Pd(C_3H_5)(C_5H_5)$ (117 mg, 0.55 mmol) was added *t*-butyl isocyanide (183 mg, 2.2 mmol) at -10°C under argon. After 30 min., removal of supernatant liquid gave **2**

as orange solid, which was washed twice with pentane, dried in vacuo, and used for further reaction in the same flask. Complex **2** was obtained nearly quantitatively, though the yield was not determined for the each reaction.

Synthesis of Complex 3a. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (106 mg, 0.5 mmol) and *t*-butyl isocyanide (166 mg, 2.0 mmol), was added **1a** (79 mg, 0.5 mmol) at room temperature under an argon atmosphere. After 10 min., evaporation of the solvent followed by washing with cold 2-propanol afforded spectroscopically pure **3a** (184 mg, 85%) as a crystalline solid. **3a:** mp 79–81°C (dec.); ^{1}H NMR (C_6D_6) δ 0.83 (s, 12 H), 1.00 (s, 18 H), 1.24–1.33 (m, 4 H), 2.47–2.51 (m, 2 H); ^{13}C NMR (C_6D_6) δ 7.1, 22.3, 22.8, 29.7, 55.8, 147.5 (br); ^{29}Si NMR (C_6D_6) δ -0.4; IR (C_6H_6) 2168, 2148 cm^{-1}. Anal. Calcd for $C_{17}H_{36}N_2PdSi_2$: C, 47.37; H, 8.42; N, 6.50. Found: C, 47.14; H, 8.59; N, 6.38.

Synthesis of Complex 3b. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **1b** (36 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 30 min., evaporation of the solvent followed by recrystallization from 2-propanol afforded **3b** (46 mg, 73%) as colorless crystals. **3b**: mp 142.0–143.5 (dec.); ^{1}H NMR (C_6D_6) δ 1.00 (s, 18 H), 1.11 (d, J = 6.5 Hz, 12 H), 1.18 (dd, J = 13.7, 7.0 Hz, 4 H), 1.27 (d, J = 6.5 Hz, 12 H), 1.44 (dd, J = 13.7, 6.4 Hz, 4 H), 2.04–2.26 (m, 4 H), 7.36–7.42 (m, 2 H), 7.80–7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.5, 27.0, 27.4, 30.4, 33.2, 56.2, 126.4, 131.2, 145.9 (br), 157.5; ^{29}Si NMR ($CDCl_3$) δ 37.3; IR (C_6H_6) 2152 cm^{-1}. Anal. Calcd for $C_{32}H_{42}N_2PdSi_2$: C, 60.68; H, 9.23; N, 4.42. Found: C, 60.70; H, 9.44; N, 4.32.

Synthesis of Complex 3d. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **1d** (20 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 30 min, evaporation of the solvent gave spectroscopically pure **3d** (46 mg, 96 %). **3d**: ^{1}H NMR (C_6D_6) δ 0.72 (s, 6 H), 1.01 (s, 18 H), 1.30–1.38 (m, 2 H), 1.58–1.66 (m, 2 H), 2.04–2.20 (m, 2 H), 2.22–2.36 (m, 2 H), 3.76 (s, 6 H); ^{13}C NMR (C_6D_6) δ 6.3, 19.9, 21.0, 25.6, 26.8, 30.0, 50.3, 55.8, 147.0 (br); ^{29}Si NMR (C_6D_6) δ 3.4, 43.3; IR (C_6H_6) 2176, 2160 cm^{-1}.

Synthesis of Complex 3e. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (42 mg, 0.2 mmol) and

t-butyl isocyanide (67 mg, 0.8 mmol), was added **1e** (59 mg, 0.2 mmol) at room temperature under an argon atmosphere. The reaction mixture was stood for 1h to precipitate crystalline **3e** containing 1 equiv of benzene (100 mg, 77%). **3e**: mp 160–165 (dec.); ^{1}H NMR (CD_2Cl_2) δ 0.25 (s, 12 H), 1.51 (s, 18 H), 3.45 (br s, 2 H), 7.04–7.08 (m, 8 H); ^{13}C NMR (CD_2Cl_2) δ 5.9 (br), 30.3, 48.5 (br), 57.0, 123.9, 125.9, 139.8, 143.7 (br); ^{29}Si NMR (CD_2Cl_2) δ -13.5; IR (KBr) 2176, 2156 cm^{-1}. Anal. Calcd for $C_{28}H_{40}N_2PdSi_2 \cdot C_6H_6$: C, 63.28; H, 7.18; N, 4.34. Found: C, 63.47; H, 7.26; N, 4.25.

2,2-Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane (4a). To a THF (20 mL) solution of 2-(1,1,2,2-tetramethyl-2-phenyldisilanyl)-1,3-dithiane, prepared quantitatively from 1,3-dithiane (1 g, 8.3 mmol), *n*-butyllithium (8.3 mmol), and 1-chloro-1,1,2,2,-tetramethyl-2-phenyldisilane (1.9 g, 8.3 mmol) in ether, was added *n*-butyllithium (8.3 mmol) at -15°C. The mixture was stirred at -15°C for 15 min. and at 0°C for 45 min., and then treated with 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (1.9 g, 8.3 mmol) in THF (10 mL). After stirring at room temperature for 2h, saturated aqueous NH_4Cl (20 mL) was added to the solution. Extractive work-up followed by column chromatography on silica gel (hexane) afforded **4a** (3.4 g, 81% from 1,3-dithiane). **4a**: mp. 50.5–51.5 °C. ^{1}H NMR (C_6D_6) δ 0.30 (s, 12 H), 0.65 (s, 12H), 1.34–1.46 (m, 2 H), 2.10–2.16 (m, 4 H), 7.16–7.28 (m, 6 H), 7.56–7.62 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -1.5, -0.7, 23.2, 23.7, 27.0, 127.5, 128.1, 134.3, 140.5; IR (KBr) 2904, 1430, 1250 cm^{-1}. Anal. Calcd for $C_{24}H_{40}S_2Si_4$: C, 57.08; H, 7.98. Found: C, 56.95; H, 8.04.

2,2-Bis(pentamethyldisilanyl)-1,3-dithiane (4g). By the procedure similar to that used for **4a**, the title compound was prepared in 80% yield from 1,3-dithiane. **4g**: ^{1}H NMR (C_6D_6) δ 0.35 (s, 18 H), 0.39 (s, 12H), 1.44–1.56 (m, 2 H), 2.25–2.32 (m, 4 H); ^{13}C NMR (C_6D_6) δ -0.6, 0.3, 23.3, 24.2, 27.1. Anal. Calcd for $C_{14}H_{36}S_2Si_4$: C, 44.14; H, 9.53. Found: C, 44.01; H, 9.61.

Synthesis of Complex 5a. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**) (ca. 0.5 mmol) was added **4a** (253 mg, 0.50 mmol) at room temperature under argon. After 10 min., pentane (4 mL) was added to the solution to precipitate colorless crystals of **5a**, which was washed with MeOH (2 mL x 3) and dried in vacuo. The complex **5a** (214 mg, 0.43 mmol, 85 %) was thermally stable under nitrogen but gradually decomposed by exposure to the air. **5a**: mp 168–170°C (dec.); ^{1}H NMR (C_6D_6) δ 0.84 (s, 18 H), 1.00 (s, 12 H), 1.96–2.09 (m, 2 H),

2.68–2.76 (m, 4 H); ^{13}C NMR (C_6D_6) δ 3.1, 27.5, 27.8, 30.0, 30.7, 55.9, 147.5 (br); ^{29}Si NMR (C_6D_6) δ -21.8; IR (C_6H_6) 2164, 2144 cm^{-1}. Anal. Calcd for $C_{18}H_{36}N_2PdS_2Si_2$: C, 42.62; H, 7.15. Found: C, 42.34; H, 7.35.

Synthesis of Complex 5c. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **4c** (42 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 6 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **5c** (30 mg, 72%), which was washed with cold 2-propanol. **5c**: mp 115–120°C (dec.); ^1H NMR (C_6D_6) δ 0.76 (s, 12 H), 0.89 (s, 18 H), 1.42 (s, 4 H); ^{13}C NMR (C_6D_6) δ 5.4, 18.7, 29.8, 55.8, 148.2 (br); ^{29}Si NMR (C_6D_6) δ 36.4; IR (C_6H_6) 2164, 2144 cm^{-1}. Anal. Calcd for $C_{16}H_{34}N_2PdSi_2$: C, 46.08; H, 8.22; N, 6.72. Found: C, 45.81; H, 8.16; N, 6.68.

Synthesis of Complex 5f. To a benzene (1 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **4f** (46 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 3.5 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **5f** (26 mg, 56%), which was washed with cold 2-propanol. **5f**: mp 145°C (dec.); ^1H NMR (C_6D_6) δ 0.86 (s, 12H), 0.93 (s, 18 H), 7.39–7.45 (m, 2 H), 7.84–7.90 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 5.5, 30.6, 57.0, 127.6, 131.0, 145.5 (br), 158.2; ^{29}Si NMR (C_6D_6) δ 30.5; IR (C_6H_6) 2168, 2148 cm^{-1}. Anal. Calcd for $C_{20}H_{34}N_2PdSi_2$: C, 51.65; H, 7.37; N, 6.02. Found: C, 51.62; H, 7.66; N, 5.74.

Synthesis of Complex 8a. To a benzene (0.5 mL) solution of bis(*t*-butyl isocyanide)palladium(0) (**2**), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **7a** (70 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 6 h, evaporation of the solvent was followed by addition of 2-propanol (0.2 mL) to precipitate crystalline **8a** (51 mg, 73%), which was washed with cold 2-propanol. **8a**: mp 162.5–164.5°C (dec.); ^1H NMR (C_6D_6) δ 0.67 (s, 18 H), 4.14 (s, 4 H), 7.16–7.32 (m, 12 H), 7.98–8.06 (m, 8 H); ^{13}C NMR (CD_2Cl_2) δ 29.8, 56.9, 66.7, 127.3, 127.8, 135.3, 143.1 (br), 146.6; IR (C_6H_6) 2180, 2170 cm^{-1}. Anal. Calcd for $C_{36}H_{42}N_2O_2PdSi_2$: C, 62.01; H, 6.07; N, 4.02. Found: C, 61.76; H, 6.08; N, 3.90.

Synthesis of Complex 8b. To a benzene (1 mL) solution of bis(*t*-butyl

isocyanide)palladium(0) (2), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **7b** (84 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 4 h, evaporation of the solvent was followed by addition of 2-propanol (0.3 mL) to precipitate crystalline **8b** (80 mg, 95%), which was washed with cold 2-propanol. **8b**: mp 148–151°C (dec.); ^{1}H NMR (C_6D_6) δ 0.63 (s, 18 H), 0.86 (t, J = 7.2 Hz, 6 H), 3.68–3.94 (m, 4 H), 5.34 (s, 2 H), 7.16–7.28 (m, 12 H), 8.10–8.16 (m, 8 H); ^{13}C NMR (CD_2Cl_2) δ 14.1, 29.8, 57.0, 60.9, 76.6, 127.3, 127.4, 127.8, 128.5, 135.1, 136.3, 142.7 (br), 143.8, 147.0, 170.6; IR (C_6H_6) 2176, 1740 cm^{-1}. Anal. Calcd for $C_{42}H_{50}N_2O_6PdSi_2$: C, 59.95; H, 5.99; N, 3.33. Found: C, 60.20; H, 6.06; N, 3.26.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3e with Cyclic Disilane 1a (Illustrated in Scheme 3). To a benzene-d_6 (0.5 mL) suspension of **3e** (0.05 mmol) in an NMR tube was added **1a** (8 mg, 0.05 mmol) at room temperature under an argon atmosphere. The mixture was heated at 50°C to dissolve **3e**. After 6h, ^{1}H NMR showed that clean disilane exchange reaction occurred to give bis(organosilyl)palladium complex **3a** and disilane **1e**.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3a with Cyclic Disilane 1b (Illustrated in Scheme 3). To a benzene-d_6 (0.5 mL) solution of **3a** (43 mg, 0.1 mmol) in an NMR tube was added **1b** (36 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 5 min, ^{1}H NMR showed that clean disilane exchange reaction occurred to give bis(organosilyl)palladium complex **3b** and disilane **1a**.

^{1}H NMR Study of the Reaction of Bis(organosilyl)palladium Complex 3a with 4g (Illustrated in eq.9). To a benzene-d_6 (0.5 mL) solution of **3a** (0.05 mmol) in an NMR tube was added **4g** (19 mg, 0.05 mmol) at room temperature under an argon atmosphere. After 18 h, ^{1}H NMR showed the formation of **5a**, **1a**, and hexamethyldisilane together with unchanged **3a** and **4g**. The ratio of **5a**, **1a**, hexamethyldisilane, **3a**, **4g** was determined to be 3 / 3 / 3 / 1 / 1.

Synthesis of Complex 9. To a benzene (1 mL) solution of **5a** (101 mg, 0.2 mmol) was added PPh_3 (52 mg, 0.2 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystallization from benzene–pentane (1 / 4) gave **9** containing 1 / 3 equiv of pentane (119 mg, 84%) as colorless crystals. **9**: mp 80.5–82.0°C; ^{1}H NMR (C_6D_6) δ 0.82 (s, 9 H), 0.83 (s, 12 H), 1.92–2.04 (m, 2 H), 2.65–2.73 (m, 4 H), 7.00–7.08 (m, 9 H), 7.56–7.68 (m, 6 H);

^{13}C NMR (CD_2Cl_2) δ 2.3, 27.6, 28.4, 30.2, 30.5, 56.7, 128.5 (d, J = 10.8 Hz), 129.5, 134.1 (d, J = 15.4 Hz), 137.0 (m), 147.0 (br); ^{29}Si NMR (C_6D_6) δ -19.3 (m); ^{31}P NMR (C_6D_6) δ 16.7 (s); IR (C_6H_6) 2956, 2152, 1437, 1095 cm^{-1}. Anal. Calcd for $C_{31}H_{42}NPPdS_2Si_2 \cdot 1/3C_5H_{12}$: C, 55.23; H, 6.52; N, 1.97. Found: C, 55.84; H, 6.65; N, 1.85.

Synthesis of Complex 10. To a benzene (1 mL) solution of **5a** (101 mg, 0.2 mmol) was added dimethylphenylphosphine (68 mg, 0.48 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystallization from benzene–pentane (1 / 10) gave **10** (104 mg, 84%) as colorless needles. **10**: mp 132.0–134.0°C (dec.); ^1H NMR (C_6D_6) δ 0.84 (s, 12 H), 1.09 (d, J = 4.7 Hz, 12 H), 1.92–2.04 (m, 2 H), 2.62–2.68 (m, 4 H), 6.98–7.06 (m, 6 H), 7.26–7.36 (m, 4 H); ^{13}C NMR (CD_2Cl_2) δ 2.7, 17.7 (d, J = 14.3 Hz), 27.5, 28.2, 30.2, 128.7 (d, J = 8.0 Hz), 129.5, 131.1 (d, J = 13.8 Hz), 140.3 (m); ^{29}Si NMR (C_6D_6) δ -18.8 (m); ^{31}P NMR (C_6D_6) δ -18.9 (s); IR (C_6H_6) 2916, 1438, 1236, 834 cm^{-1}. Anal. Calcd for $C_{24}H_{40}P_2PdS_2Si_2$: C, 46.70; H, 6.53. Found: C, 47.20; H, 6.57.

Synthesis of Complex 11. To a benzene (1 mL) solution of **3b** (63 mg, 0.1 mmol) was added 1,2-bis(diphenylphosphino)ethane (40 mg, 0.1 mmol) at room temperature under an argon atmosphere. After 10 min, evaporation of the solvent followed by recrystallization from CH_2Cl_2–2-propanol (1 / 3) gave **11** (79 mg, 91%) as colorless crystals. **11**: mp 196°C (dec.); ^1H NMR (C_6D_6) δ 0.83 (dd, J = 13.9, 4.8 Hz, 4 H), 0.95 (d, J = 6.3 Hz, 24 H), 1.06–1.22 (m, 4 H), 1.64–1.72 (m, 2 H), 1.78–1.86 (m, 2 H), 1.96–2.18 (m, 4 H), 7.10–7.20 (m, 12 H), 7.32–7.36 (m, 2 H), 7.54–7.66 (m, 8 H), 7.78–7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1, 26.8, 27.6, 27.8 (t, J = 18.0 Hz), 32.6 (t, J = 5.7 Hz), 126.1, 128.5 (m), 130.0, 132.1, 133.5 (m), 134.4 (m), 157.4 (t, J = 3.9 Hz); ^{29}Si NMR ($CDCl_3$) δ 39.2 (dd, J = 128, 13 Hz); ^{31}P NMR (C_6D_6) δ 30.8; IR (KBr) 3040, 2952, 1438, 1100, 742 cm^{-1}. Anal. Calcd for $C_{48}H_{64}P_2PdSi_2$: C, 66.61; H, 7.45. Found: C, 66.38; H, 7.64.

Stoichiometric Reaction of the Complex 5a with Phenylacetylene. To a solution of **5a** (13.2 mg, 0.026 mmol) in benzene-d_6 (0.5 mL) was added phenylacetylene (3.1 mg, 0.030 mmol) at room temperature. After 5 min, the reaction mixture was subjected to preparative TLC (hexane / ether = 10 / 1) to furnish **12a** (8.6 mg, 98 %). **12a**; mp. 53.5–54.5 °C. ^1H NMR ($CDCl_3$) δ 0.46 (s, 6 H), 0.50 (s, 6H), 1.96–2.12 (m, 2 H), 2.68–2.76 (m, 4 H), 6.90 (s, 1 H), 7.20–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -0.8, -0.6, 22.9, 25.6, 28.8, 126.2, 127.2, 128.3, 142.6, 145.4, 163.3;

IR (KBr) 2960, 1490, 1252 cm^{-1}. Anal. Calcd for $C_{16}H_{24}S_2Si_2$: C, 57.08; H, 7.19. Found: C, 56.93; H, 7.28.

Stoichiometric Reaction of the Complex 5a with Trimethylsilylacetylene. To a solution of **5a** (58 mg, 0.11 mmol) in toluene (1 mL) was added trimethylsilylacetylene (17 mg, 0.17 mmol) at room temperature. After 8 h, the reaction mixture was subjected to column chromatography on silica gel (hexane / ether = 10 / 1) to furnish **13** (33 mg, 90 %). ^1H NMR-monitoring showed the reaction completed within 3.5 h. **13**; mp. 53.0–53.5 °C. ^1H NMR (C_6D_6) δ 0.14 (s, 9 H), 0.46 (s, 6 H), 0.54 (s, 6 H), 1.56–1.76 (m, 2 H), 2.24–2.46 (m, 4 H), 7.59 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.8, -0.6, -0.4, 22.7, 25.7, 28.9, 163.5, 171.7; IR (neat) 2964, 1250, 832 cm^{-1}. Anal. Calcd for $C_{13}H_{28}S_2Si_3$: C, 46.94; H, 8.48. Found: C, 46.99; H, 8.70.

Stoichiometric Reaction of the Complex 5a with Dimethyl Acetylenedicarboxylate. To a solution of **5a** (16 mg, 0.032 mmol) in benzene-d_6 (0.5 mL) was added dimethyl acetylenedicarboxylate (4.5 mg, 0.032 mmol) at room temperature. Within 10 min, bis-silylation completed to form bis(*t*-butyl isocyanide)(**14**)palladium(0) complexes, from which **14** was liberated by addition of dimethyl acetylenedicarboxylate (9 mg, 0.064 mmol). The reaction mixture was stirred for 2 h, and then subjected to column chromatography on silica gel (CH_2Cl_2) to furnish **14** (12 mg, 99 %). **14**; ^1H NMR (C_6D_6) δ 0.57 (s, 12 H), 1.50–1.60 (m, 2 H), 2.16–2.24 (m, 4 H), 3.42 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ -1.7, 21.8, 25.2, 28.9, 52.0, 156.2, 168.5; IR (neat) 2960, 1726, 1240 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_4S_2Si_2$: C, 44.65; H, 6.42. Found: C, 44.48; H, 6.32.

Stoichiometric Reaction of the Complex 5a with Diphenylacetylene. To a solution of **5a** (46 mg, 0.091 mmol) in toluene (1 mL) was added diphenylacetylene (24 mg, 0.14 mmol) at room temperature. After 12 h at 90 °C, the reaction mixture was subjected to preparative TLC (hexane / ether = 10 / 1) to furnish **15** (36 mg, 96 %). **15**; mp. 162–163 °C. ^1H NMR (C_6D_6) δ 0.53 (s, 12 H), 1.64–1.74 (m, 2 H), 2.34–2.40 (m, 4 H), 6.84–7.02 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ -1.2, 22.1, 25.6, 28.8, 125.5, 127.7, 141.4, 158.1; IR (KBr) 2920, 1482, 1248 cm^{-1}. Anal. Calcd for $C_{22}H_{28}S_2Si_2$: C, 64.03; H, 6.84. Found: C, 63.92; H, 6.87.

Reaction of 4b and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (0.9 mg, 4 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (8.4 mg, 0.06 mmol) in toluene (0.3 mL) were added **4b** (80 mg, 0.20 mmol) and phenylacetylene (61 mg, 0.60 mmol) under an

argon atmosphere. The mixture was stirred at 90°C for 7h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12b** (2 mg, 4%), **16b** (48 mg, 48%), and **17b** (34 mg, 28%). **16b** and **17b** consisted of two and three regio isomers, respectively, and the isomers could not be separated by preparative GLC nor by preparative gel permeation chromatography (GPC) from each other.

12b; ^{1}H NMR ($CDCl_3$) δ -0.15 (s, 2 H), 0.20 (s, 6H), 0.30 (s, 6 H), 7.02 (s, 1 H), 7.20–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -2.1, 0.4, 1.1, 126.3, 126.9, 128.3, 143.0, 148.5, 165.8. Anal. Calcd for $C_{13}H_{20}Si_2$: C, 67.17; H, 8.67. Found: C, 67.03; H, 8.77.

16b; ^{1}H NMR for the major isomer ($CDCl_3$) δ 0.22 (s, 2 H), 0.00 (s, 12 H), 0.32 (s, 6H), 0.33 (s, 6H), 6.63 (s, 1H), 7.04–7.10 (m, 2 H), 7.16–7.46 (m, 11 H), 7.54–7.60 (m, 2 H). MS (20 eV) *m/z* 502 (M^+). Anal. Calcd for $C_{29}H_{42}Si_4$: C, 69.25; H, 8.42. Found: C, 68.95; H, 8.37.

17b; ^{1}H NMR for the major isomer ($CDCl_3$) δ -0.30 (s, 2 H), -0.03 (s, 12 H), 0.30 (s, 12 H), 6.57 (s, 2 H), 6.98–7.06 (m, 4 H), 7.16–7.36 (m, 12 H), 7.50–7.60 (m, 4 H). MS (20 eV) *m/z* 604 (M^+). Anal. Calcd for $C_{37}H_{48}Si_4$: C, 73.44; H, 7.99. Found: C, 73.29; H, 8.16.

Reaction of 4h and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (4.5 mg, 0.02 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (42 mg, 0.30 mmol) in toluene (1 mL) were added **4h** (83 mg, 0.20 mmol) and phenylacetylene (61 mg, 0.60 mmol) under an argon atmosphere. The mixture was stirred at 90°C for 7h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12h** (33 mg, 67%) and **16h** (19 mg, 18%).

12h; ^{1}H NMR ($CDCl_3$) δ 0.11 (q, J = 7.8 Hz, 1 H), 0.13 (s, 3H), 0.19 (s, 3 H), 0.25 (s, 3 H), 0.27 (s, 3 H), 1.11 (d, J = 7.8 Hz, 3 H), 7.01 (s, 1 H), 7.16–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -3.2, -2.5, -0.5, 0.0, 3.4, 8.3, 126.2, 126.9, 128.3, 143.1, 147.7, 165.3; IR (neat) 2960, 1490, 1250, 852, 778 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00. Found: C, 68.40; 9.28.

16h; ^{1}H NMR for major isomer (500 MHz, $CDCl_3$) δ -0.10 (s, 6H), -0.02 (q, J = 7.6 Hz, 1 H), 0.018 (s, 3H), 0.024 (s, 3 H), 0.25 (s, 3 H), 0.28 (s, 3 H), 0.31 (s, 3 H), 0.32 (s, 3 H), 0.92 (d, J = 7.6 Hz, 3 H), 6.55 (s, 1 H), 6.99–7.02 (m, 2 H), 7.11–7.23 (m, 3 H), 7.27–7.32 (m, 6 H), 7.40–7.42 (m, 2 H), 7.49–7.52 (m, 2 H). MS (20 eV) *m/z* 516 (M^+). Anal. Calcd for $C_{30}H_{44}Si_4$: C, 69.69; H, 8.58. Found: C, 69.55; H, 8.48.

Reaction of 4i and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4i** (78 mg, 0.16 mmol) with phenylacetylene was carried out to give **12i** (47 mg, 91%).

12i: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.37 (s, 3H), 0.38 (s, 3 H), 0.41 (s, 3 H), 4.00 (s, 1 H), 6.86–7.00 (m, 3 H), 7.01 (s, 1 H), 7.24–7.40 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ -3.5, -2.9, -0.2, -0.1, 62.2, 114.6, 119.8, 126.3, 127.3, 128.4, 129.2, 142.7, 146.2, 161.6, 164.3; IR (neat) 2968, 1600, 1490, 1238, 858 cm^{-1}. Anal. Calcd for $C_{19}H_{24}OSi_2$: C, 70.31; H, 7.45. Found: C, 70.22; H, 7.51.

Reaction of 4j and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4j** (102 mg, 0.2 mmol) with phenylacetylene was carried out to give **12j** (66 mg, 97%).

12j: ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 3 H), 0.30 (s, 3H), 0.35 (s, 6 H), 2.02 (s, 1 H), 7.00 (s, 1 H), 7.08–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ -2.5, -1.8, 0.5, 0.8, 13.5, 125.0, 126.2, 127.3, 127.6, 128.4, 128.5, 140.2, 142.5, 147.0, 164.9; IR (neat) 3064, 2968, 1586, 1482, 1252, 860 cm^{-1}. Anal. Calcd for $C_{19}H_{24}SSi_2$: C, 67.00; H, 7.10. Found: C, 67.05; H, 7.13.

Reaction of 4a and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, reaction of **4a** (202 mg, 0.40 mmol) with phenylacetylene was carried out to give **12a** (123 mg, 91%).

Reaction of 4c and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4c** (83 mg, 0.20 mmol) with phenylacetylene was carried out to give **12c** (19 mg, 39%), **16c** (16 mg, 15%), and **17c** (37 mg, 30%).

12c; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H), 0.15 (s, 6H), 0.84–0.98 (m, 4 H), 6.60 (s, 1 H), 7.16–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -2.1, -1.8, 7.0, 8.8, 126.2, 128.1, 145.9, 147.3, 161.8; IR (neat) 2908, 1490, 1250, 832, 776 cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$: C, 68.22; H, 9.00. Found: C, 68.29; H, 8.98.

16c; ^{1}H NMR for major isomer ($CDCl_3$) δ -0.08 (s, 6 H), -0.01 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.37–0.44 (m, 4 H), 6.59 (s, 1H), 7.02–7.08 (m, 2 H), 7.14–7.46 (m, 11 H), 7.56–7.61 (m, 2 H). MS (20 eV) *m/z* 516 (M^+). Anal. Calcd for $C_{30}H_{44}Si_4$: C, 69.69; H, 8.58. Found: C, 69.52; H, 8.64.

17c; ^{1}H NMR for major isomer ($CDCl_3$) δ -0.09 (s, 12 H), 0.32 (s, 12 H), 0.28–0.36 (m, 4 H), 6.60 (s, 2 H), 7.02–7.08 (m, 4 H), 7.16–7.36 (m, 12 H), 7.54–7.60 (m, 4 H). MS (20 eV) *m/z* 618 (M^+). Anal. Calcd for $C_{38}H_{50}Si_4$: C, 73.72; H, 8.14. Found: C, 73.42; H, 8.35.

Reaction of 4d and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4d** (86 mg, 0.20 mmol) with phenylacetylene was carried out to give **16d** (53 mg, 50%) and **17d** (42 mg, 33%).

16d; ^{1}H NMR for major isomer ($CDCl_3$) δ -0.09 (s, 6 H), 0.02 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.43–0.63 (m, 4 H), 1.16–1.34 (m, 2 H), 6.57 (s, 1 H), 7.00–7.06 (m, 2 H), 7.14–7.38 (m, 9 H), 7.39–7.45 (m, 2 H), 7.54–7.60 (m, 2 H). MS (20 eV) *m/z* 530 (M^+). Anal. Calcd for $C_{31}H_{46}Si_4$: C, 70.11; H, 8.73. Found: C, 70.34; H, 8.88.

17d; ^{1}H NMR for major isomer ($CDCl_3$) δ -0.06 (s, 12 H), 0.32 (s, 12 H), 0.43–0.55 (m, 4 H), 1.16–1.36 (m, 2 H), 6.59 (s, 2 H), 7.01–7.07 (m, 4 H), 7.16–7.36 (m, 12 H), 7.54–7.60 (m, 4 H). MS (20 eV) *m/z* 632 (M^+). Anal. Calcd for $C_{39}H_{52}Si_4$: C, 73.98; H, 8.28. Found: C, 74.04; H, 8.51.

Reaction of 4e and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. By a procedure similar to that used for the reaction of **4b**, the reaction of **4e** (89 mg, 0.20 mmol) with phenylacetylene was carried out to give **16e** (41 mg, 38%) and **17e** (64 mg, 49%).

16e: ^{1}H NMR for major isomer ($CDCl_3$) δ -0.06 (s, 6 H), 0.02 (s, 6 H), 0.32 (s, 6H), 0.33 (s, 6H), 0.38–0.58 (m, 4 H), 1.16–1.28 (m, 4 H), 6.60 (s, 1H), 7.04–7.10 (m, 2 H), 7.16–7.38 (m, 9 H), 7.40–7.46 (m, 2 H), 7.56–7.62 (m, 2 H). MS (20 eV) *m/z* 544 (M^+). Anal. Calcd for $C_{32}H_{48}Si_4$: C, 70.51; H, 8.88. Found: C, 70.74; H, 9.16.

17e; ^{1}H NMR for major isomer ($CDCl_3$) δ 0.06 (s, 12 H), 0.32 (s, 12 H), 0.38–0.46 (m, 4 H), 1.14–1.26 (m, 4 H), 6.60 (s, 2 H), 7.04–7.08 (m, 4 H), 7.16–7.28 (m, 6 H), 7.30–7.36 (m, 6 H), 7.54–7.60 (m, 4 H). MS (20 eV) *m/z* 646 (M^+). Anal. Calcd for $C_{40}H_{54}Si_4$: C, 74.23; H, 8.41. Found: C, 73.94; H, 8.58.

Reactions of 16c and Phenylacetylene Catalyzed by *t*-Octyl Isocyanide–Palladium(II) Acetate. To a mixture of palladium(II) acetate (0.4 mg, 1.8 μmol) and 1,1,3,3-tetramethylbutyl isocyanide (3.7 mg, 0.027 mmol) in toluene (0.1 mL) were added **16c** (46 mg, 0.09 mmol) and phenylacetylene (14 mg, 0.14 mmol) under an argon atmosphere. The mixture was stirred at 90°C for 7h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **17c** (20 mg, 36%)

and recovered **16c** (27 mg, 59%).

Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)phenoxymethane (4i). To a THF (20 mL) solution of phenoxy(1,1,2,2-tetramethyl-2-phenyldisilanyl)methane (150 mg, 0.5 mmol), prepared from phenoxymethyllithium and 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane in 75% yield,[31] was added *sec*-butyllithium (1.1 M in cyclohexane, 0.54 mmol) at -78°C. The mixture was allowed to warm to -25°C and held at the temperature for 0.5 h. To the mixture cooled to -40°C was added 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane (114 mg, 0.5 mmol). The mixture was allowed to warm to room temperature over 1.5 h, and then saturated aqueous NH_4Cl was added. Extractive workup followed by purification by preparative TLC gave **4i** (78 mg, 32 %). **4i**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6 H), 0.11 (s, 6 H), 0.20 (s, 6 H), 0.23 (s, 6 H), 4.12 (s, 1 H), 6.68–6.74 (m, 2 H), 6.76–6.86 (m, 1 H), 7.08–7.18 (m, 2 H), 7.26–7.36 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ -3.9, -3.8, -3.5, -2.9, 62.3, 114.6, 119.4, 127.7, 128.3, 129.1, 133.9, 139.3, 160.3. Anal. Calcd for $C_{27}H_{40}OSi_4$: C, 65.79; H, 8.18. Found: C, 65.57; H, 8.23.

Bis(1,1,2,2-tetramethyl-2-phenyldisilanyl)phenylthiomethane (4j). To a THF (10 mL) solution of (phenylthio)(1,1,2,2-tetramethyl-2-phenyldisilanyl)methane (1 g, 3.2 mmol), prepared from (phenylthio)methyllithium and 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane, was added n-butyllithium (1.6 M in hexane, 3.1 mmol) at 0°C. After 1.5 h, 1-chloro-1,1,2,2-tetramethyl-2-phenyldisilane was added dropwise, and the mixture was stirred for 16 h at room temperature. The reaction was quenched by addition of saturated aqueous NH_4Cl. Extractive workup followed by purification by preparative gel permeation chromatography gave **4j** (670 mg, 42 %). **4j**: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 6 H), 0.11 (s, 6 H), 0.30 (s, 6 H), 0.31 (s, 6 H), 1.74 (s, 1 H), 6.84–6.88 (m, 2 H), 6.98–7.16 (m, 3 H), 7.24–7.40 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ -3.2, -2.9, -2.6, -1.1, 12.4, 124.2, 126.1, 127.7, 128.3, 128.4, 138.9, 139.4, 139.7. Anal. Calcd for $C_{27}H_{40}SSi_4$: C, 63.71; H, 7.92. Found: C, 63.62; H, 7.96.

^{1}H NMR Study of the Catalytic Cycle of the Bis-Silylation via Intramolecular Metathesis (Illustrated in Scheme 5). To a benzene-d_6 (0.5 mL) solution of **5a** (9.5 mg, 0.019 mmol) in an NMR tube was added phenylacetylene (1.9 mg, 0.019 mmol) at room temperature under an argon atmosphere. ^{1}H NMR showed clean formation of (bis-silylated alkene)palladium complex **18** after 1 min. To the mixture was added **4g** (7.2 mg, 0.019 mmol). Monitoring the reaction by ^{1}H NMR revealed

that formation of **5a**, hexamethyldisilane, and bis-silylated alkene **12a** from **18** and **4g** completed after 3.5h at room temperature. **18** was identified by comparison with the authentic sample, which was prepared by mixing isolated **12a** with bis(*t*-butyl isocyanide)palladium(0) (**2**) in benzene-d_6 .

General Procedure for the Catalytic Bis-Silylation of Alkynes with 4g in the Presence of 5a. To a mixture of **4g** (152 mg, 0.40 mmol) and **5a** (4.0 mg, 8.0 μmol) in toluene (0.4 mL) was added alkynes (0.60 mmol) under an argon atmosphere. The mixture was stirred under the conditions listed in Table 3, cooled to room temperature, and then subjected to preparative TLC (for **12a,13,15**,and **19**), or bulb-to-bulb distillation (for **20**) to furnish the cyclized product.

19: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 6 H), 0.36 (s, 6 H), 0.88 (t, J = 6.2 Hz, 3 H), 1.24–1.50 (m, 8 H), 1.96–2.08 (m, 2 H), 2.18–2.28 (m, 2 H), 2.64–2.72 (m, 4 H), 6.40 (t, J = 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -1.5, -0.7, 14.1, 22.6, 22.8, 25.7, 28.3, 28.9, 29.1, 31.7, 37.2, 141.8, 166.9; IR (neat) 2932, 1250, 860 cm^{-1}. Anal. Calcd for $C_{16}H_{32}S_2Si_2$: C, 55.75; H, 9.36. Found: C, 55.83; H, 9.60.

20: mp. 46.0–46.5°C. ^{1}H NMR (C_6D_6) δ 0.44 (s, 6 H), 0.51 (s, 6 H), 0.81 (t, J = 7.0 Hz, 3 H), 1.08–1.42 (m, 4 H), 1.56–1.72 (m, 2 H), 2.03 (s, 3 H), 2.18–2.38 (m, 6 H); ^{13}C NMR (C_6D_6) δ -1.3, -0.6, 14.0, 22.4, 23.1, 25.7, 28.8, 31.4, 32.0, 33.5, 160.0, 160.2, 206.3; IR (neat) 2964, 1682, 1252, 1202, 836 cm^{-1}. Anal. Calcd for $C_{16}H_{30}OS_2Si_2$: C, 53.57; H, 8.43. Found: C, 53.41; H, 8.66.

General Procedure for the Catalytic Bis-Silylation of Alkenes with 4g in the Presence of 5a. To a mixture of **4g** (152 mg, 0.40 mmol) and **5a** (4.0 mg, 8.0 μmol) in toluene (0.4 mL) was added alkenes (0.60 mmol) under an argon atmosphere. The mixture was stirred at 90°C for 15h, cooled to room temperature, and then subjected to preparative TLC (for **21a** and **22a–c**), or bulb-to-bulb distillation (for **21b**) to furnish the cyclized product.

21a; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3 H), 0.31 (s, 3 H), 0.37 (s, 3 H), 0.50 (s, 3 H), 1.04 (dd, J = 7.3, 15.0 Hz, 1 H), 1.31 (dd, J = 11.9, 15.0 Hz, 1 H), 1.96–2.06 (m, 2 H), 2.40 (dd, J = 7.3, 11.9 Hz, 1 H), 2.56–2.80 (m, 4 H), 3.65 (s, 3 H); ^{13}C NMR (C_6D_6) δ -3.9, -1.9, -1.4, -0.6, 12.1, 22.9, 25.6, 28.6, 28.7, 31.3, 50.9, 175.4; IR (neat) 2960, 1728, 1252, 1192, 858 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_2S_2Si_2$: C, 44.95; H, 7.55. Found: C, 44.88; H, 7.77.

21b; mp. 75.0–76.5 °C. ^{1}H NMR (C_6D_6) δ 0.09 (s, 3 H), 0.19 (s, 3 H), 0.31 (s, 3 H), 0.42 (s, 3H), 0.78 (dd, J = 12.0, 14.9 Hz, 1 H), 0.92 (dd, J = 7.6, 14.9 Hz, 1 H),

1.38–1.58 (m, 2 H), 1.72 (dd, J = 7.6, 12.0 Hz, 1 H), 2.00–2.30 (m, 4 H); ^{13}C NMR (C_6D_6) δ -4.0, -2.6, -1.9, -1.5, 11.8, 13.8, 21.7, 25.3, 28.5, 28.7, 122.4; IR (neat) 2964, 2220, 1420, 1256, 802 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NS_2Si_2$: C, 45.94; H, 7.36; N, 4.87. Found: C, 45.78; H, 7.39; N, 4.70.

22a; ^{1}H NMR (C_6D_6) δ 0.42 (s, 6 H), 0.55 (s, 6 H), 1.40–1.58 (m, 4 H), 1.73 (d, J = 1.1 Hz, 3 H), 2.12–2.38 (m, 4 H), 4.64 (tq, J = 6.8, 1.1 Hz, 1H); ^{13}C NMR (C_6D_6) δ -1.8, 0.5, 12.8, 22.7, 24.9, 25.0, 26.9, 103.8, 148.1; IR (neat) 2924, 1678, 1252, 1004 cm^{-1}. Anal. Calcd for $C_{12}H_{24}OS_2Si_2$: C, 47.31; H, 7.94. Found: C, 47.26; H, 8.20.

22b; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 3 H), 0.34 (s, 3 H), 0.41 (s, 3 H), 0.51 (s, 3 H), 1.02 (d, J =7.7 Hz, 3 H), 1.74 (dd, J = 1.5, 1.1 Hz, 3 H), 1.80–2.16 (m, 3 H), 2.50–2.84 (m, 4 H), 4.40 (dq, J = 5.9, 1.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -5.5, -3.4, -0.4, 1.7, 15.7, 16.8, 22.4, 22.6, 24.8, 26.6, 26.8, 113.0, 145.6; IR (neat) 2960, 1676, 1252, 832 cm^{-1}. Anal. Calcd for $C_{13}H_{26}OS_2Si_2$: C, 49.00; H, 8.22. Found: C, 48.70; H, 8.39.

22c; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 6 H), 0.46 (s, 6 H), 1.75 (d, J = 7.4 Hz, 2 H), 1.86–2.10 (m, 2 H), 2.56–2.82 (m, 4 H), 5.71 (t, J = 7.4 Hz, 1 H), 7.20–7.34 (m, 3 H), 7.46–7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -2.1, 0.1, 13.3, 24.5, 24.7, 26.7, 105.7, 123.9, 127.0, 128.1, 137.6, 148.7; IR (KBr) 2968, 1682, 1254, 1080, 848 cm^{-1}. Anal. Calcd for $C_{17}H_{26}OS_2Si_2$: C, 55.68; H, 7.15. Found: C, 55.41; H, 7.18.

Single Crystal X-ray Analysis of 5a and 11. Suitable single crystals of **5a** and **11** were grown from benzene–pentane (1/4) and from benzene–ethanol (2/1) at ambient temperature, respectively. A crystal of **5a** coated with silicon grease was mounted in a thin-walled glass capillary under argon atmosphere. A crystal of **11** was mounted on a glass fiber using epoxy resin. Data collection were carried out on a Mac Science MXC3 diffractmeter with Mo Kα radiation (λ = 0.70930 Å) for **5a** and Cu Kα radiation (λ = 1.54178 Å) for **11**. For **5a**, the intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 8.70 cm^{-1}). For **11**, the intensity data were corrected for Lorentzian polarization and empirical absorption correction based on azimuthal scans of several reflections. The structures were solved by direct methods and refined full-matrix least-squares procedure against $|F^2|$ (for **5a**) and against $|F|$ (for **11**) with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for that on C(19) in **5a** were located on a difference electron density map and refined with isotropic thermal parameters calculated

from those of the bonded atoms. Hydrogen atoms in **11** were partially included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 4. Final positional parameters for **5a** and **11** are listed in Table 5 and 9, respectively. Anisotropic thermal parameters for **5a** and **11** are given in Table 6 and 10, respectively. Intramolecular bond distances for **5a** and **11** are presented in Table 7 and 11, respectively. Intramolecular bond angles for **5a** and **11** are presented in Table 8 and 12, respectively.

Table 4. Summary of Crystallographic Data for **5a** and **11**

compound	**5a**	**11**
formula	$C_{18}H_{36}N_2PdS_2Si_2$	$C_{48}H_{64}P_2PdSi_2$
formula weight	507.2	865.6
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (No. 14)
a, Å	8.257 (1)	23.312 (6)
b, Å	10.829 (3)	18.541 (4)
c, Å	15.360 (3)	11.094 (4)
α, deg	94.14 (2)	
β, deg	99.72 (2)	97.62 (2)
γ, deg	101.92 (2)	
cell vol, Å^3	1316.2 (4)	4753 (2)
Z	2	4
ρ(calcd), g cm^{-3}	1.28	1.21
F(000)	528	1824
crystal size, mm	0.35 × 0.15 × 0.30	0.55 × 0.40 × 0.30
μ, cm^{-1}	8.70	45.73
diffractometer	Mac Science MXC3	Mac Science MXC3
monochromator	graphite	graphite
radiation	Mo Kα (λ = 0.70930 Å)	Cu Kα (λ = 1.54178 Å)
temp, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
2θmax, deg	50	130
reflns measured	4792	8826
independent reflns	4389	7945
reflns used	4135	5348
no. of variables	337	500
R, Rw	0.048, 0.048	0.062, 0.086
goodness of fit	1.16	1.68
max δ/σ in final cycle	1.40	3.37
residual electron density (min, max) (e/Å^3)	-0.64, 0.58	-0.59, 1.20

Table 5. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$) with Esd's in Parentheses for **5a**

atom	x	y	z	B(eq)
Pd1	0.01396(4)	0.06601(3)	0.20950(2)	4.70(3)
Si2	0.2099(1)	0.2595(1)	0.22613(9)	5.17(4)
Si3	0.2371(1)	0.0819(1)	0.33067(8)	4.53(4)
S 4	0.4711(1)	0.3602(1)	0.40326(8)	5.70(4)
S 5	0.5587(1)	0.2038(1)	0.25751(8)	5.93(4)
N 6	-0.1973(5)	0.1558(4)	0.0412(3)	5.9(1)
N 7	-0.1744(4)	-0.2049(3)	0.2527(2)	5.3(1)
C 8	0.3936(4)	0.2336(3)	0.3139(3)	4.3(1)
C 9	0.6267(7)	0.2950(6)	0.4720(4)	6.9(2)
C 10	0.7644(7)	0.2682(6)	0.4247(4)	7.4(2)
C 11	0.7058(6)	0.1657(6)	0.3488(4)	7.1(2)
C 12	0.1260(8)	0.3934(6)	0.2722(6)	8.8(2)
C 13	0.2824(8)	0.3089(8)	0.1218(5)	9.4(2)
C 14	0.1669(8)	0.1057(7)	0.4389(4)	7.4(2)
C 15	0.3294(8)	-0.0632(5)	0.3365(5)	7.1(2)
C 16	-0.1312(6)	0.1146(4)	0.1008(3)	5.7(1)
C 17	-0.1129(5)	-0.1090(4)	0.2325(3)	5.4(1)
C 18	-0.2711(6)	0.2161(5)	-0.0322(3)	6.2(2)
C 19	-0.151(1)	0.227(1)	-0.0974(5)	11.2(3)
C 20	-0.284(1)	0.3466(8)	0.0081(6)	10.9(3)
C 21	-0.442(1)	0.1328(9)	-0.0736(5)	10.2(3)
C 22	-0.2462(6)	-0.3267(4)	0.2813(3)	5.4(1)
C 23	-0.4122(8)	-0.3173(6)	0.3074(6)	8.9(2)
C 24	-0.268(1)	-0.4273(6)	0.2026(5)	8.6(2)
C 25	-0.1230(9)	-0.3501(6)	0.3595(5)	7.9(2)
H 9A	0.564(7)	0.214(6)	0.486(4)	6.87(0)
H 9B	0.673(8)	0.351(6)	0.522(4)	6.87(0)
H 10A	0.848(8)	0.238(6)	0.466(4)	7.30(0)
H 10B	0.831(8)	0.347(6)	0.408(4)	7.30(0)
H 11A	0.783(8)	0.152(6)	0.325(4)	6.78(0)
H 11B	0.646(7)	0.077(6)	0.363(4)	6.78(0)
H 12A	0.204(9)	0.470(7)	0.264(4)	8.67(0)
H 12B	0.035(9)	0.392(6)	0.229(5)	8.67(0)
H 12C	0.115(9)	0.386(7)	0.335(5)	8.67(0)
H 13A	0.369(9)	0.384(7)	0.128(5)	9.34(0)
H 13B	0.32(1)	0.236(7)	0.095(5)	9.34(0)
H 13C	0.20(1)	0.302(7)	0.079(5)	9.34(0)
H 14A	0.071(8)	0.045(6)	0.441(4)	7.20(0)
H 14B	0.249(8)	0.104(6)	0.488(4)	7.20(0)
H 14C	0.140(8)	0.180(6)	0.450(4)	7.20(0)
H 15A	0.397(8)	-0.056(6)	0.392(4)	6.86(0)
H 15B	0.244(8)	-0.138(6)	0.337(4)	6.86(0)
H 15C	0.382(8)	-0.065(6)	0.302(5)	6.86(0)
H 19A	-0.19(1)	0.277(8)	-0.136(6)	10.77(0)
H 19B	-0.05(1)	0.267(8)	-0.070(6)	10.77(0)
H 20A	-0.38(1)	0.304(7)	0.049(6)	10.42(0)
H 20B	-0.15(1)	0.390(8)	0.027(6)	10.42(0)
H 20C	-0.34(1)	0.384(8)	-0.041(6)	10.42(0)
H 21A	-0.49(1)	0.175(7)	-0.124(5)	10.19(0)
H 21B	-0.52(1)	0.124(8)	-0.034(6)	10.19(0)
H 21C	-0.39(1)	0.051(7)	-0.104(5)	10.19(0)
H 23A	-0.457(8)	-0.386(7)	0.335(5)	8.46(0)

H 23B	-0.487(9)	-0.306(7)	0.262(5)	8.46(0)
H 23C	-0.385(8)	-0.236(7)	0.359(5)	8.46(0)
H 24A	-0.157(9)	-0.436(7)	0.190(5)	8.55(0)
H 24B	-0.352(9)	-0.406(7)	0.158(5)	8.55(0)
H 24C	-0.318(9)	-0.501(7)	0.224(5)	8.55(0)
H 25A	-0.027(8)	-0.368(6)	0.331(4)	7.74(0)
H 25B	-0.158(8)	-0.433(7)	0.375(4)	7.74(0)
H 25C	-0.113(8)	-0.282(6)	0.409(4)	7.74(0)

Table 6. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **5a**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Pd1	0.058(1)	0.0507(2)	0.0623(2)	0.0044(1)	0.0036(2)	0.0170(2)
Si2	0.057(1)	0.0556(7)	0.0767(8)	0.0060(5)	0.0030(5)	0.0288(6)
Si3	0.060(1)	0.0491(6)	0.0577(7)	0.0100(5)	0.0090(5)	0.0174(5)
S 4	0.074(1)	0.0562(6)	0.0778(8)	0.0116(5)	0.0062(6)	0.0033(5)
S 5	0.068(1)	0.0826(8)	0.0718(8)	0.0210(6)	0.0239(6)	0.0195(6)
N 6	0.076(2)	0.078(2)	0.061(2)	0.018(2)	0.003(2)	0.013(2)
N 7	0.071(2)	0.047(2)	0.077(2)	0.004(2)	0.014(2)	0.007(2)
C 8	0.054(2)	0.047(2)	0.058(2)	0.010(2)	0.011(2)	0.012(2)
C 9	0.087(4)	0.096(4)	0.068(3)	0.018(3)	-0.012(3)	0.006(3)
C 10	0.064(3)	0.106(4)	0.101(4)	0.019(3)	-0.006(3)	0.023(4)
C 11	0.063(3)	0.100(4)	0.105(4)	0.034(3)	0.018(3)	0.027(3)
C 12	0.083(4)	0.061(3)	0.176(7)	0.027(3)	-0.013(4)	0.008(4)
C 13	0.088(4)	0.155(6)	0.096(5)	-0.016(4)	-0.001(3)	0.076(5)
C 14	0.086(4)	0.119(5)	0.066(3)	0.006(3)	0.024(3)	0.021(3)
C 15	0.093(4)	0.063(3)	0.107(5)	0.025(3)	0.007(3)	0.033(3)
C 16	0.069(3)	0.068(3)	0.070(3)	0.003(2)	-0.001(2)	0.015(2)
C 17	0.064(3)	0.058(3)	0.074(3)	0.007(2)	0.006(2)	0.011(2)
C 18	0.095(3)	0.078(3)	0.055(3)	0.027(2)	0.005(2)	0.019(2)
C 19	0.126(6)	0.21(1)	0.080(5)	0.031(6)	0.029(4)	0.049(5)
C 20	0.181(8)	0.102(5)	0.124(6)	0.056(5)	0.026(6)	0.019(4)
C 21	0.108(5)	0.154(7)	0.102(6)	0.000(5)	-0.025(4)	0.047(5)
C 22	0.074(3)	0.043(2)	0.079(3)	0.008(2)	0.010(2)	0.011(2)
C 23	0.094(4)	0.090(4)	0.156(7)	0.023(3)	0.051(4)	0.058(4)
C 24	0.136(6)	0.057(3)	0.117(5)	0.006(3)	0.009(4)	-0.006(3)
C 25	0.115(5)	0.080(4)	0.094(4)	0.027(3)	-0.005(4)	0.017(3)

Table 7. Intramolecular Distances (Å) with Esd's in Parentheses for **5a**

atom	atom	distance	atom	atom	distance
Pd1	- Si2	2.336(1)	Pd1	- Si3	2.356(1)
Pd1	- C 16	2.053(5)	Pd1	- C 17	2.053(4)
Si2	- Si3	2.613(2)	Si2	- C 8	1.933(4)
Si2	- C 12	1.875(7)	Si2	- C 13	1.878(8)
Si3	- C 8	1.931(4)	Si3	- C 14	1.868(7)
Si3	- C 15	1.884(7)	N 6	- C 16	1.151(6)
N 6	- C 18	1.451(6)	N 7	- C 17	1.146(6)
N 7	- C 22	1.460(5)	S 4	- C 8	1.801(4)
S 4	- C 9	1.813(6)	S 5	- C 8	1.803(4)
S 5	- C 11	1.824(6)	C 9	- C 10	1.512(9)
C 10	- C 11	1.492(8)	C 18	- C 21	1.514(8)
C 18	- C 19	1.52(1)	C 18	- C 20	1.53(1)
C 22	- C 25	1.509(8)	C 22	- C 23	1.512(9)
C 22	- C 24	1.528(8)			

Table 8. Intramolecular Angles (deg) with Esd's in Parentheses for **5a**

atom	atom	atom	angle	atom	atom	atom	angle
Si2	- Pd1	- Si3	67.68(4)	Si2	- Pd1	- C 16	92.0(1)
Si2	- Pd1	- C 17	161.9(1)	Si3	- Pd1	- C 16	159.7(1)
Si3	- Pd1	- C 17	94.4(1)	C 16	- Pd1	- C 17	105.9(2)
Pd1	- Si2	- C 8	103.0(1)	Pd1	- Si2	- C 12	111.6(2)
Pd1	- Si2	- C 13	115.5(2)	C 8	- Si2	- C 12	108.5(3)
C 8	- Si2	- C 13	111.8(2)	C 12	- Si2	- C 13	106.4(4)
Pd1	- Si3	- C 8	102.3(1)	Pd1	- Si3	- C 14	111.4(2)
Pd1	- Si3	- C 15	114.1(2)	C 8	- Si3	- C 14	109.5(2)
C 8	- Si3	- C 15	114.0(2)	C 14	- Si3	- C 15	105.6(3)
C 8	- S 4	- C 9	100.3(2)	C 8	- S 5	- C 11	101.1(2)
C 16	- N 6	- C 18	175.8(4)	C 17	- N 7	- C 22	177.5(4)
Pd1	- C 16	- N 6	171.3(4)	Pd1	- C 17	- N 7	173.8(4)
S 4	- C 8	- S 5	111.8(2)	Si2	- C 8	- S 4	114.4(2)
Si2	- C 8	- S 5	108.3(2)	Si3	- C 8	- S 4	119.9(2)
Si3	- C 8	- S 5	114.1(2)	Si2	- C 8	- Si3	85.1(1)
S 4	- C 9	- C 10	113.3(4)	S 5	- C 11	- C 10	113.8(5)
C 9	- C 10	- C 11	114.4(4)	N 6	- C 18	- C 19	106.7(5)
N 6	- C 18	- C 20	106.0(5)	N 6	- C 18	- C 21	108.2(5)
N 7	- C 22	- C 23	107.6(4)	N 7	- C 22	- C 24	106.7(4)
N 7	- C 22	- C 25	107.8(4)	C 19	- C 18	- C 20	111.9(6)
C 20	- C 18	- C 21	112.3(6)	C 21	- C 18	- C 19	111.4(5)
C 23	- C 22	- C 24	112.2(5)	C 24	- C 22	- C 25	111.0(5)
C 25	- C 22	- C 23	111.2(5)				

Table 9. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **11**

atom	x/a	y/b	z/c	U(iso)
Pd1	0.40305(3)	0.20789(4)	0.67018(8)	0.050
P 2	0.47591(13)	0.21691(17)	0.54147(32)	0.061
P 3	0.38076(13)	0.09818(16)	0.56585(32)	0.060
Si4	0.33990(14)	0.19628(18)	0.82038(33)	0.060
Si5	0.40981(13)	0.32675(17)	0.74893(31)	0.057
C 6	0.3369(5)	0.2803(7)	0.9161(12)	0.066
C 7	0.3647(5)	0.3422(7)	0.8782(12)	0.064
C 8	0.3616(6)	0.4071(8)	0.9397(14)	0.081
C 9	0.3341(8)	0.4126(12)	1.0391(19)	0.106
C 10	0.3095(7)	0.3526(14)	1.0801(15)	0.113
C 11	0.3092(7)	0.2870(9)	1.0207(15)	0.089
C 12	0.2625(6)	0.1752(9)	0.7450(16)	0.087
C 13	0.2144(10)	0.1516(23)	0.8260(33)	0.212
C 14	0.17314	0.20862	0.86974	0.787
C 15	0.18064	0.08772	0.76034	0.473
C 16	0.3612(7)	0.1177(8)	0.9244(14)	0.083
C 17	0.4229(10)	0.1106(12)	0.9844(19)	0.118
C 18	0.4281(12)	0.0399(14)	1.0642(24)	0.156
C 19	0.4486(14)	0.1762(17)	1.0526(27)	0.177
C 20	0.4855(8)	0.3592(13)	0.8064(17)	0.115
C 21	0.5219(11)	0.3354(32)	0.9204(35)	0.286
C 22	0.57928	0.37140	0.89641	0.386
C 23	0.51618	0.39170	1.02151	0.342
C 24	0.3866(6)	0.3938(7)	0.6241(13)	0.070
C 25	0.3366(8)	0.3762(8)	0.5243(15)	0.089
C 26	0.2799(8)	0.3669(11)	0.5802(17)	0.108
C 27	0.3304(10)	0.4353(10)	0.4199(17)	0.114
C 28	0.4606(6)	0.1468(8)	0.4222(14)	0.080
C 29	0.4418(6)	0.0786(7)	0.4814(14)	0.078
C 30	0.4919(6)	0.2962(7)	0.4546(15)	0.077
C 31	0.5355(7)	0.3445(9)	0.5023(17)	0.093
C 32	0.5414(10)	0.4085(10)	0.4384(25)	0.124
C 33	0.5061(14)	0.4261(14)	0.3367(28)	0.147
C 34	0.4636(12)	0.3796(13)	0.2893(20)	0.131
C 35	0.4555(8)	0.3151(11)	0.3495(19)	0.106
C 36	0.5465(6)	0.1857(7)	0.6164(14)	0.070
C 37	0.5515(7)	0.1635(9)	0.7333(16)	0.087
C 38	0.6044(9)	0.1365(10)	0.7946(21)	0.107
C 39	0.6515(8)	0.1345(10)	0.7311(28)	0.117
C 40	0.6464(8)	0.1584(12)	0.6095(26)	0.124
C 41	0.5948(6)	0.1846(10)	0.5530(18)	0.089
C 42	0.3224(5)	0.1106(7)	0.4425(13)	0.071
C 43	0.2926(6)	0.1754(8)	0.4342(15)	0.080
C 44	0.2483(9)	0.1873(13)	0.3393(23)	0.122
C 45	0.2369(9)	0.1370(15)	0.2466(22)	0.129
C 46	0.2659(10)	0.0742(13)	0.2544(19)	0.121
C 47	0.3093(8)	0.0596(10)	0.3501(16)	0.099
C 48	0.3662(5)	0.0110(7)	0.6320(13)	0.068
C 49	0.3114(6)	-0.0186(8)	0.6216(14)	0.077
C 50	0.3023(9)	-0.0821(10)	0.6819(20)	0.105
C 51	0.3462(11)	-0.1164(10)	0.7496(21)	0.119
C 52	0.3997(9)	-0.0870(11)	0.7632(18)	0.109

C 53	0.4116(7)	-0.0245(8)	0.7058(17)	0.088
H 8	0.37923	0.44952	0.91108	0.08(4)
H 9	0.33147	0.45780	1.08018	0.08(4)
H 10	0.29148	0.35542	1.15292	0.11(5)
H 11	0.29084	0.24507	1.04927	0.11(6)
H 12A	0.26517	0.13669	0.68811	0.06(4)
H 12B	0.24757	0.21739	0.70151	0.14(8)
H 16A	0.35204	0.07450	0.87819	0.09(5)
H 16B	0.33744	0.12020	0.98849	0.06(3)
H 20	0.48249	0.41062	0.81341	0.3(2)
H 24A	0.42001	0.40258	0.58397	0.11(6)
H 24B	0.37631	0.43757	0.66197	0.3(2)
H 28A	0.49442	0.13853	0.38333	0.07(4)
H 28B	0.42962	0.16273	0.36243	0.09(5)
H 29A	0.43037	0.04248	0.42092	0.14(8)
H 29B	0.47387	0.06078	0.53662	0.07(4)
H 31	0.56013	0.33230	0.57585	0.10(6)
H 32	0.57149	0.44128	0.47066	0.10(5)
H 33	0.51118	0.47115	0.29704	0.16(9)
H 35	0.42474	0.28331	0.31728	0.08(5)
H 37	0.51795	0.16585	0.77510	0.2(1)
H 38	0.60803	0.12022	0.87738	0.2(1)
H 39	0.68779	0.11640	0.77071	0.14(8)
H 40	0.68020	0.15696	0.56853	0.13(7)
H 41	0.59118	0.19952	0.46946	0.5(4)
H 43	0.30207	0.21137	0.49584	0.08(4)
H 44	0.22609	0.23098	0.33558	0.14(7)
H 45	0.20746	0.14586	0.17908	0.17(9)
H 46	0.25683	0.03944	0.19056	0.14(7)
H 47	0.33016	0.01488	0.35378	0.09(5)
H 49	0.28011	0.00481	0.57146	0.07(4)
H 50	0.26414	-0.10228	0.67501	0.13(7)
H 51	0.33940	-0.16040	0.79101	0.12(6)
H 52	0.43075	-0.11108	0.81280	0.13(7)
H 53	0.44986	-0.00451	0.71439	0.07(4)

T=exp[-2π²U], U=U(iso) or [U(11)+U(22)+U(33)]/3

Table 10. Anisotropic Thermal Parameters (Å²) with Esd's in Parentheses for **11**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	U11	U22	U33	U12	U13	U23
Pd1	0.0326(5)	0.0526(5)	0.0637(6)	-0.0018(3)	0.0041(3)	-0.0030(3)
P 2	0.041(1)	0.063(2)	0.077(2)	-0.004(1)	0.011(1)	-0.005(1)
P 3	0.041(1)	0.054(2)	0.082(2)	-0.003(1)	0.004(1)	-0.010(1)
Si4	0.040(2)	0.069(2)	0.068(2)	-0.004(1)	0.005(1)	0.001(1)

Si5	0.043(2)	0.057(2)	0.070(2)	-0.004(1)	0.003(1)	-0.006(1)
C 6	0.040(6)	0.086(9)	0.071(8)	0.009(5)	0.011(5)	-0.014(6)
C 7	0.041(6)	0.081(8)	0.069(7)	0.002(6)	0.000(5)	-0.021(6)
C 8	0.060(8)	0.092(10)	0.088(10)	0.001(7)	0.001(7)	-0.032(8)
C 9	0.07(1)	0.13(1)	0.12(1)	0.00(1)	0.00(1)	-0.06(1)
C 10	0.06(1)	0.19(2)	0.08(1)	0.00(1)	0.01(1)	-0.06(1)
C 11	0.052(8)	0.119(13)	0.092(10)	-0.006(8)	0.017(7)	-0.022(9)
C 12	0.061(9)	0.095(11)	0.102(11)	-0.017(8)	-0.001(8)	0.011(9)
C 13	0.06(1)	0.32(4)	0.26(4)	-0.06(2)	-0.02(2)	-0.09(3)
C 14	0.25(6)	0.31(7)	1.76(36)	0.13(5)	0.42(13)	0.57(14)
C 15	0.33(8)	0.45(9)	0.62(12)	-0.20(7)	0.32(9)	-0.21(9)
C 16	0.078(9)	0.087(10)	0.081(9)	0.010(8)	0.010(8)	0.022(8)
C 17	0.11(2)	0.13(2)	0.11(1)	0.01(1)	-0.02(1)	0.04(1)
C 18	0.15(2)	0.14(2)	0.17(2)	0.03(2)	-0.02(2)	0.07(2)
C 19	0.20(3)	0.15(2)	0.17(3)	0.03(2)	-0.09(2)	0.01(2)
C 20	0.07(1)	0.17(2)	0.10(1)	-0.05(1)	0.01(1)	-0.05(1)
C 21	0.06(1)	0.53(7)	0.26(4)	-0.05(3)	-0.05(2)	-0.12(5)
C 22	0.20(4)	0.69(13)	0.25(5)	-0.18(7)	-0.07(4)	-0.02(7)
C 23	0.19(4)	0.71(12)	0.12(2)	0.12(6)	-0.02(2)	-0.12(5)
C 24	0.076(9)	0.065(7)	0.068(7)	0.002(6)	-0.001(7)	-0.001(6)
C 25	0.10(1)	0.07(1)	0.09(1)	0.02(1)	0.00(1)	0.01(1)
C 26	0.08(1)	0.13(2)	0.11(1)	0.01(1)	0.01(1)	-0.01(1)
C 27	0.14(2)	0.10(1)	0.10(1)	0.03(1)	0.01(1)	0.02(1)
C 28	0.064(8)	0.088(9)	0.087(10)	-0.009(7)	0.017(8)	-0.027(8)
C 29	0.059(8)	0.076(8)	0.096(10)	-0.007(6)	0.019(7)	-0.030(8)
C 30	0.057(8)	0.072(8)	0.100(10)	-0.007(6)	0.033(8)	-0.008(7)
C 31	0.07(1)	0.08(1)	0.12(1)	-0.01(1)	0.03(1)	0.00(1)
C 32	0.11(2)	0.08(1)	0.18(2)	-0.02(1)	0.05(2)	0.01(1)
C 33	0.14(2)	0.12(2)	0.17(2)	0.01(2)	0.05(2)	0.06(2)
C 34	0.15(2)	0.13(2)	0.11(2)	0.03(2)	0.04(1)	0.05(1)
C 35	0.09(1)	0.12(1)	0.11(1)	-0.01(1)	0.01(1)	0.03(1)
C 36	0.051(7)	0.066(7)	0.091(10)	-0.003(6)	0.007(6)	-0.001(6)
C 37	0.069(9)	0.089(10)	0.101(11)	-0.006(8)	-0.005(8)	0.023(9)
C 38	0.09(1)	0.10(1)	0.13(2)	0.01(1)	-0.02(1)	0.01(1)
C 39	0.06(1)	0.09(1)	0.19(2)	0.01(1)	-0.03(1)	0.00(1)
C 40	0.052(9)	0.130(16)	0.186(23)	0.014(10)	0.006(12)	-0.029(16)
C 41	0.052(8)	0.101(10)	0.110(12)	0.002(7)	0.008(8)	-0.019(9)
C 42	0.048(7)	0.069(8)	0.092(9)	-0.008(6)	0.001(6)	-0.002(6)
C 43	0.065(9)	0.082(9)	0.089(10)	0.001(7)	0.002(7)	-0.002(8)
C 44	0.08(1)	0.13(2)	0.15(2)	0.03(1)	-0.03(1)	0.03(1)
C 45	0.10(1)	0.17(2)	0.12(2)	-0.02(1)	-0.06(1)	0.03(1)
C 46	0.12(2)	0.12(2)	0.11(1)	-0.03(1)	-0.05(1)	-0.02(1)
C 47	0.09(1)	0.09(1)	0.11(1)	-0.02(1)	-0.01(1)	-0.02(1)
C 48	0.053(7)	0.059(6)	0.090(9)	-0.007(5)	0.001(6)	-0.004(6)
C 49	0.052(7)	0.076(8)	0.102(10)	-0.012(6)	0.000(7)	0.010(7)
C 50	0.08(1)	0.09(1)	0.14(2)	-0.01(1)	0.00(1)	0.02(1)
C 51	0.13(2)	0.08(1)	0.14(2)	-0.03(1)	0.00(1)	0.02(1)
C 52	0.11(1)	0.10(1)	0.11(1)	0.03(1)	0.00(1)	0.03(1)
C 53	0.072(9)	0.070(8)	0.118(12)	-0.002(7)	-0.006(9)	0.004(8)

Table 11. Intramolecular Distances (Å) with Esd's in Parentheses for **11**

atom	atom	distance	atom	atom	distance
Pd1	- P 2	2.365(4)	Pd1	- P 3	2.364(4)
Pd1	- Si4	2.375(4)	Pd1	- Si5	2.368(4)
P 2	- C 30	1.823(15)	P 2	- C 36	1.836(14)
P 2	- C 28	1.855(16)	P 3	- C 42	1.812(14)
P 3	- C 48	1.825(13)	P 3	- C 29	1.840(15)
Si4	- C 6	1.891(14)	Si4	- C 12	1.926(16)
Si4	- C 16	1.884(16)	Si5	- C 7	1.908(13)
Si5	- C 20	1.893(19)	Si5	- C 24	1.886(14)
C 10	- C 9	1.36(4)	C 10	- C 11	1.38(3)
C 39	- C 38	1.38(4)	C 39	- C 40	1.41(5)
C 32	- C 31	1.40(3)	C 32	- C 33	1.34(4)
C 30	- C 31	1.41(3)	C 30	- C 35	1.39(3)
C 36	- C 37	1.35(3)	C 36	- C 41	1.40(3)
C 9	- C 8	1.35(3)	C 6	- C 7	1.410(19)
C 6	- C 11	1.41(3)	C 7	- C 8	1.39(3)
C 42	- C 43	1.38(2)	C 42	- C 47	1.40(3)
C 48	- C 49	1.381(19)	C 48	- C 53	1.41(3)
C 37	- C 38	1.42(3)	C 41	- C 40	1.37(3)
C 25	- C 24	1.53(3)	C 25	- C 26	1.54(3)
C 25	- C 27	1.59(3)	C 12	- C 13	1.59(4)
C 28	- C 29	1.52(3)	C 49	- C 50	1.38(3)
C 16	- C 17	1.51(3)	C 43	- C 44	1.39(3)
C 20	- C 21	1.49(5)	C 18	- C 17	1.58(4)
C 47	- C 46	1.39(3)	C 52	- C 53	1.37(3)
C 52	- C 51	1.35(4)	C 50	- C 51	1.35(4)
C 44	- C 45	1.39(4)	C 33	- C 34	1.36(4)
C 34	- C 35	1.40(4)	C 17	- C 19	1.51(4)
C 46	- C 45	1.34(4)	C 13	- C 14	1.55(4)
C 13	- C 15	1.55(4)	C 22	- C 21	1.55(4)
C 21	- C 23	1.55(5)			

Table 12. Intramolecular Angles (deg) with Esd's in Parentheses for **11**

atom	atom	atom	angle	atom	atom	atom	angle
P 2	- Pd1	- P 3	83.9(2)	P 2	- Pd1	- Si4	172.5(2)
P 2	- Pd1	- Si5	98.0(2)	P 3	- Pd1	- Si4	98.6(2)
P 3	- Pd1	- Si5	168.8(2)	Si4	- Pd1	- Si5	80.9(2)
Pd1	- P 2	- C 30	126.1(5)	Pd1	- P 2	- C 36	112.1(5)
Pd1	- P 2	- C 28	107.2(5)	C 30	- P 2	- C 36	105.1(7)
C 30	- P 2	- C 28	102.8(7)	C 36	- P 2	- C 28	100.2(7)
Pd1	- P 3	- C 42	110.8(5)	Pd1	- P 3	- C 48	127.3(5)
Pd1	- P 3	- C 29	106.5(5)	C 42	- P 3	- C 48	104.8(6)
C 42	- P 3	- C 29	101.2(7)	C 48	- P 3	- C 29	103.1(7)
Pd1	- Si4	- C 6	113.1(5)	Pd1	- Si4	- C 12	110.3(6)
Pd1	- Si4	- C 16	111.2(6)	C 6	- Si4	- C 12	108.0(7)
C 6	- Si4	- C 16	108.6(7)	C 12	- Si4	- C 16	105.4(8)

Pd1	- Si5	- C 7	113.6(5)	Pd1	- Si5	- C 20	115.7(8)
Pd1	- Si5	- C 24	110.1(5)	C 7	- Si5	- C 20	106.3(7)
C 7	- Si5	- C 24	108.7(6)	C 20	- Si5	- C 24	101.6(9)
C 9	- C 10	- C 11	122.4(17)	C 38	- C 39	- C 40	120.5(20)
C 31	- C 32	- C 33	122.7(22)	P 2	- C 30	- C 31	120.2(13)
P 2	- C 30	- C 35	120.1(13)	C 31	- C 30	- C 35	119.0(15)
P 2	- C 36	- C 37	119.2(12)	P 2	- C 36	- C 41	120.5(13)
C 37	- C 36	- C 41	120.3(15)	C 10	- C 9	- C 8	118.7(19)
Si4	- C 6	- C 7	116.8(10)	Si4	- C 6	- C 11	126.2(11)
C 7	- C 6	- C 11	117.0(13)	Si5	- C 7	- C 6	115.0(10)
Si5	- C 7	- C 8	124.6(11)	C 6	- C 7	- C 8	120.2(12)
P 3	- C 42	- C 43	118.7(11)	P 3	- C 42	- C 47	122.4(12)
C 43	- C 42	- C 47	118.6(14)	P 3	- C 48	- C 49	122.5(11)
P 3	- C 48	- C 53	118.8(10)	C 49	- C 48	- C 53	118.5(13)
C 9	- C 8	- C 7	121.8(16)	C 36	- C 37	- C 38	121.7(16)
C 36	- C 41	- C 40	119.3(19)	C 24	- C 25	- C 26	110.1(14)
C 24	- C 25	- C 27	111.6(14)	C 26	- C 25	- C 27	111.8(16)
Si4	- C 12	- C 13	120.1(16)	P 2	- C 28	- C 29	108.4(11)
C 48	- C 49	- C 50	119.8(15)	C 39	- C 38	- C 37	117.7(21)
P 3	- C 29	- C 28	110.1(10)	Si4	- C 16	- C 17	119.8(13)
C 42	- C 43	- C 44	120.2(16)	C 10	- C 11	- C 6	119.8(16)
Si5	- C 20	- C 21	126.2(21)	C 42	- C 47	- C 46	119.5(17)
C 32	- C 31	- C 30	117.7(18)	C 53	- C 52	- C 51	122.1(19)
C 49	- C 50	- C 51	121.2(18)	C 48	- C 53	- C 52	118.8(16)
C 52	- C 51	- C 50	119.5(19)	Si5	- C 24	- C 25	120.5(10)
C 39	- C 40	- C 41	120.5(19)	C 43	- C 44	- C 45	120.3(21)
C 32	- C 33	- C 34	120.2(24)	C 33	- C 34	- C 35	119.5(23)
C 30	- C 35	- C 34	120.8(19)	C 16	- C 17	- C 18	108.5(18)
C 16	- C 17	- C 19	116.3(20)	C 18	- C 17	- C 19	113.1(20)
C 47	- C 46	- C 45	121.8(21)	C 44	- C 45	- C 46	119.3(22)
C 12	- C 13	- C 14	120.2(28)	C 12	- C 13	- C 15	107.3(23)
C 14	- C 13	- C 15	111.7(14)	C 20	- C 21	- C 22	97.7(27)
C 20	- C 21	- C 23	108.7(33)	C 22	- C 21	- C 23	89.6(26)

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Chapter 3

Double Oxidative Addition of the Si–Si and Si–Ge σ-Bonds onto Isonitrile–Platinum(0) Complexes Leading to the Formation of Tetrakis(organosilyl)- and Bis(organogermyl)bis(organosilyl)platinum(IV) Complexes

Abstract: Tetrakis(organosilyl)bis(*t*-butyl isocyanide)platinum(IV) complex was prepared by the reaction of 2,2-bis(disilanyl)dithiane with $Pt_3(CNBu^t)_6$ through double oxidative addition of the two Si–Si bonds onto the platinum atom. On the other hand, the reaction of hexamethyldisilane with $Pt_3(CNBu^t)_6$ or $Pt_3(CNAd)_6$ (Ad = 1-adamantyl) gave only the corresponding bis(trimethylsilyl)bis(*t*-alkyl isocyanide)platinum(II), which did not undergo further oxidative addition with hexamethyldisilane. Also, two Si–Ge bonds of 2,2-bis(silylgermyl)dithiane reacted with $Pd(CNBu^t)_2$ and $Pt_3(CNBu^t)_6$ to give bis(organogermyl)bis(*t*-butyl isocyanide)palladium(II) and bis(organogermyl)bis(organosilyl)bis(*t*-butyl isocyanide)platinum(IV) complexes, respectively, the latter being accompanied by the formation of a tetrakis(organogermyl)platinum(IV) complex. X-Ray diffraction studies of the tetrakis(organosilyl)- and tetrakis(organogermyl)-platinum(IV) complexes revealed octahedral structures, in which two isocyanide ligands occupied apical positions in a trans fashion. A crystal structure of the bis(organogermyl)palladium(II) complex was also established by an X-ray analysis.

Introduction

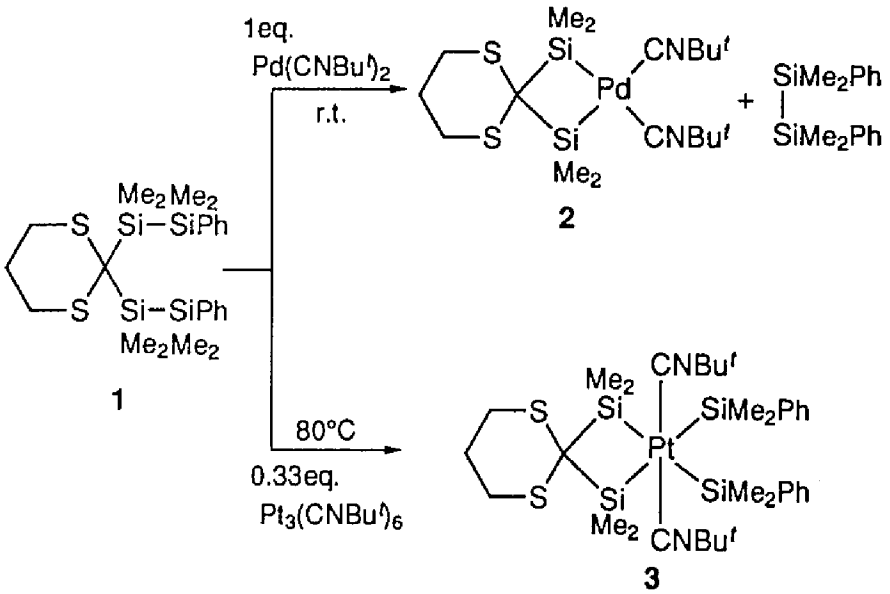
In chapter 2, the author described that bis(*t*-alkyl isocyanide)palladium(0) complexes mediated intramolecular metathesis of two Si–Si bonds oriented appropriately in a molecule to give cyclic bis(organosilyl)palladium(II) complexes.[1] For

the metathesis, the author presumed involvement of 5-centered intermediate or transition state, in which the four silicon atoms are equally coordinated with the palladium atom. The author, in this chapter, describes isolation of tetrakis(organosilyl)bis(*t*-butyl isocyanide)platinum(IV) complex, which may be relevant to the intermediate proposed for the palladium-mediated metathesis, in the reaction of 2,2-bis(disilanyl)dithiane with $Pt_3(CNBu^t)_6$. Also, the author found that two Si–Ge bonds of 2,2-bis(silylgermyl)dithiane reacted similarly with isonitrile–palladium(0) and –platinum(0) complexes to give bis(organogermyl)bis(*t*-butyl isocyanide)-palladium(II) and bis(organogermyl)bis(organosilyl)bis(*t*-butyl isocyanide)-platinum(IV) complexes, respectively, the latter being accompanied by the formation of a tetrakis(organogermyl)platinum(IV) complex.

Results and Discussion

2,2-Bis(disilanyl)dithiane **1**, which gave 4-membered bis(organosilyl)-palladium(II) **2** in the reaction with $Pd(CNBu^t)_2$, was stirred for 24 h in benzene under reflux in the presence of stoichiometric amount of $Pt_3(CNBu^t)_6$ (Scheme 1). The reaction was monitored by ^1H NMR, revealing that the starting **1** was gradually consumed and new signals similar to those for **2** appeared. The reaction mixture was chromatographed on silica gel to afford tetrakis(organosilyl)bis(*t*-butyl isocyanide)platinum(IV) complex **3** in 27% yield.

Scheme 1.



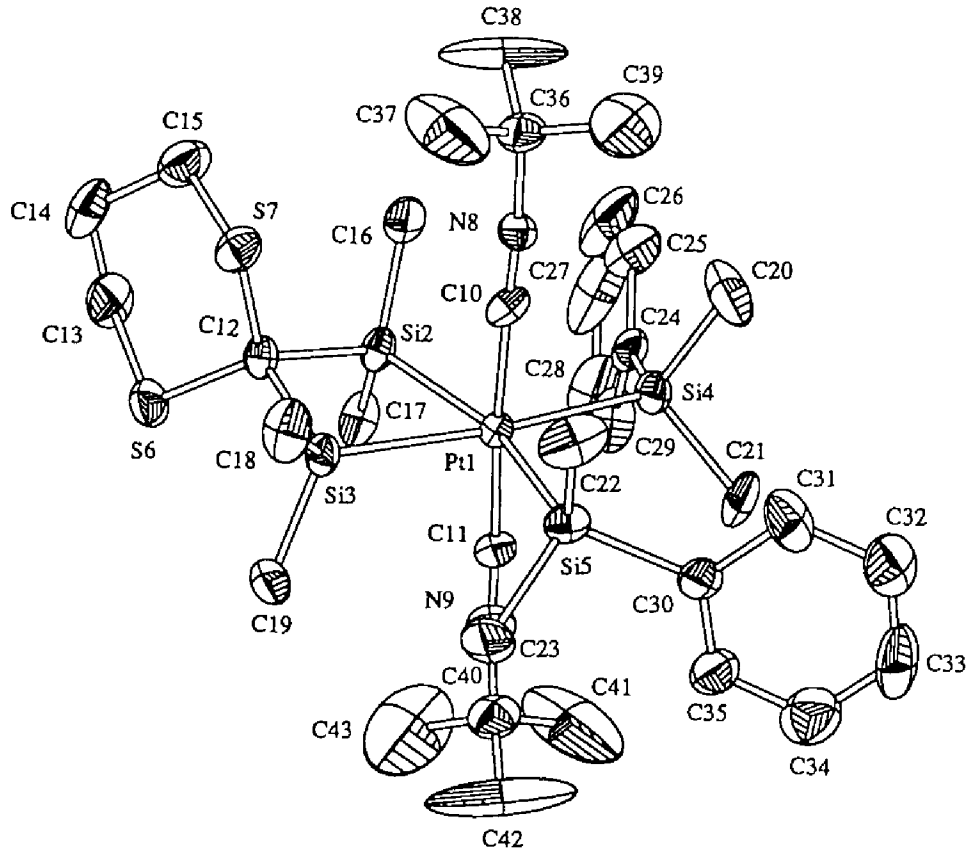


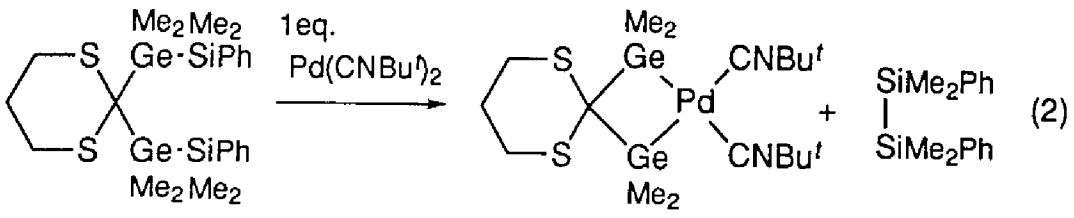
Figure 1. Crystal structure of **3**. The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances and angles are follows: Pt(1)–Si(2) = 2.493(7), Pt(1)–Si(3) = 2.457(6), Pt(1)–Si(4) = 2.482(7), Pt(1)–Si(5) = 2.470(7), Pt(1)–C(10) = 1.94(3), Pt(1)–C(11) = 1.896(1); Si(2)–Pt(1)–Si(3) = 68.6(2), Si(2)–Pt(1)–Si(4) = 99.5(3), Si(3)–Pt(1)–Si(5) = 93.0(3), Si(4)–Pt(1)–Si(5) = 98.8(3), Si(2)–Pt(1)–C(10) = 89.2(6), Si(2)–Pt(1)–C(11) = 92.5(2).

The formation of **3** may arise from double oxidative addition of two Si–Si bonds of **1** onto the platinum(0) complex. No complex corresponding to **3** formed when **1** was reacted with a $Pt(PPh_3)_2(CH_2{=}CH_2)$ complex at 50°C to 80°C. The crystal structure is shown in Figure 1 with selected bond distances and angles. In the octahedral complex, two isocyanide ligands occupied apical positions and the four silyl ligands lay at the vertices of a distorted square with the platinum atom at the center. Interestingly, the trans orientation of the isocyanide ligands is contrasted with the cis coordination of the phosphine ligands in the closely related tetrakis-(organosilyl)platinum(IV) complex which was recently reported by Tanaka et al.[2]

The author found that a reaction of $Pt_3(CNAd)_6$ (Ad = 1-adamantyl) with an excess (30 equiv) of hexamethyldisilane in benzene at 80°C gave bis(trimethylsilyl)-bis(1-adamantyl isocyanide)platinum(II) complex **4** in high yield (eq 1).[3] This result indicates that the formation of the platinum(IV) complex in the reaction of bis(disilanyl)dithiane **1** may be driven by the appropriate orientation of the two Si–Si bonds in **1** for a simultaneous interaction with the platinum atom.

$$Pt_3(CNAd)_6 \xrightarrow[\text{benzene, 80°C}]{\text{30 eq } Me_3Si{-}SiMe_3} (Me_3Si)_2Pt(CNAd)_2 \quad \textbf{4}\ (93\%) \qquad (1)$$

Next, the reactions of bis(silylgermyl)dithiane with palladium– and platinum–isonitrile complexes are remarked, since the activation of Si–Ge bonds by transition metal complexes has been scarcely studied. A reaction of 2,2-bis[dimethyl(dimethylphenylsilyl)germyl]dithiane (**5**) with $Pd(CNBu^t)_2$ gave 4-membered bis(organogermyl)palladium(II) **6** quantitatively (eq 2). Though a formation of a similar 4-membered bis(organogermyl)(phosphine)palladium(II) complex was reported in the reaction of highly strained digermirane with $Pd(PPh_3)_4$, the X-ray structural analysis has not been achieved due to instability of the complex toward the irradiation.[4] In contrast, addition of pentane into the reaction mixture gave crystals



5 **6** (2)

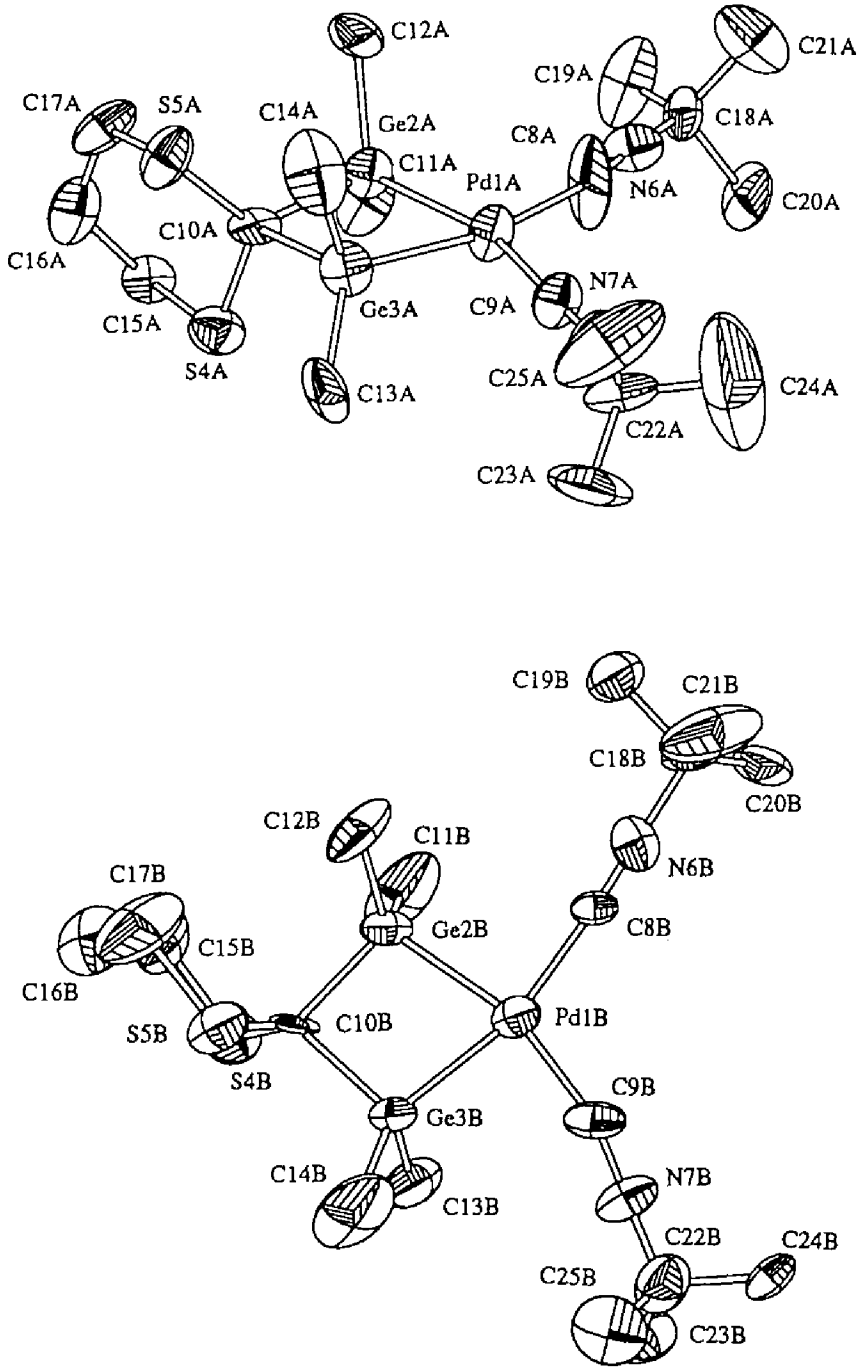
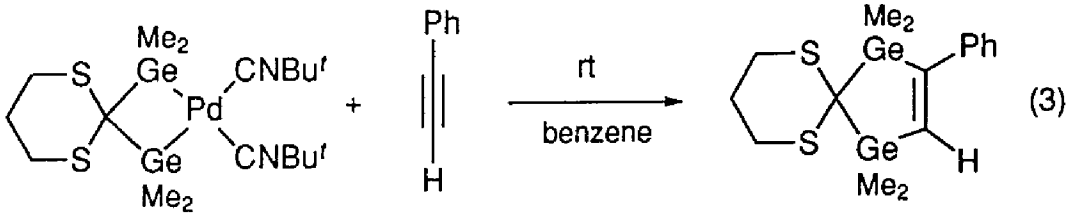


Figure 2. Crystal Structure of **6**. (Molecule A, top and Molecule B, bottom) The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

of complex **6** suitable for X-ray structure analysis revealing two crystallographically independent molecules as shown in Figure 2. The structure was similar to that of the silicon analog **2**, in which two isocyanides coordinated with relatively large angle (C(8A)–Pd(1A)–C(9A) = 109.9(18), C(8B)–Pd(1B)–C(9B) = 104.0(14)) .

As expected, the reaction of the bis(organogermyl)palladium(II) complex **6** thus isolated with phenylacetylene proceeded immediately at room temperature to obtain bis-germylated cyclic olefin **7** in high yield (eq 3).

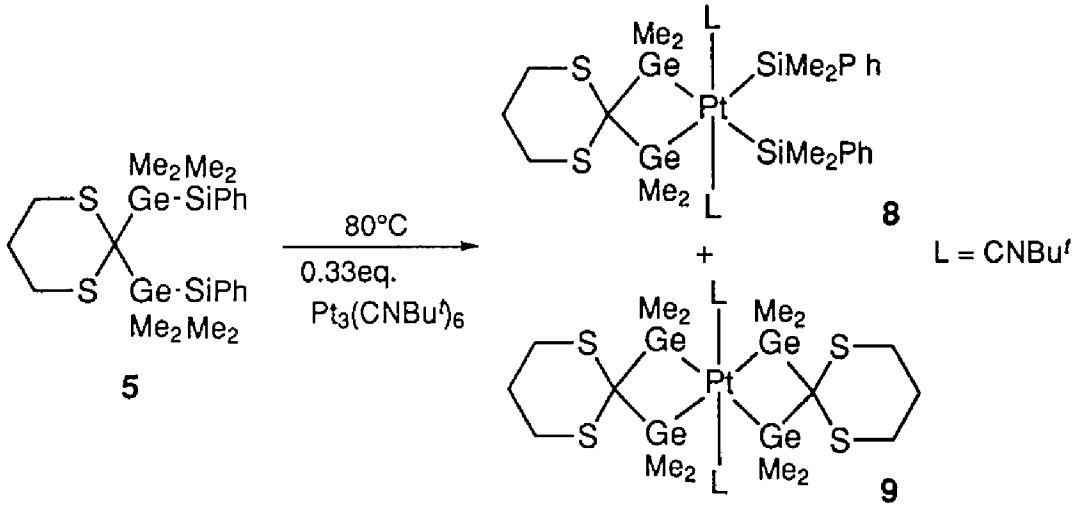


(3)

6 **7** (89%)

Furthermore, bis(silylgermane) **5** gave bis(organosilyl)bis(organogermyl)-platinum(IV) complex **8** in 30% yield in the reaction with $Pt_3(CNBu^t)_6$ (Scheme 2). It is remarked that tetrakis(organogermyl)platinum(IV) complex **9** was also obtained as a by-product, but in low yield (11%) (Figure 3).

Scheme 2.



The formation of the platinum(IV) complexes in the reaction of bis(disilane) **1** and bis(silylgermane) **5** with the platinum(0)–isonitrile complex may be suggestive of involvement of the corresponding palladium complexes in the palladium-mediated intramolecular metathesis of the Si–Si and Si–Ge bonds.

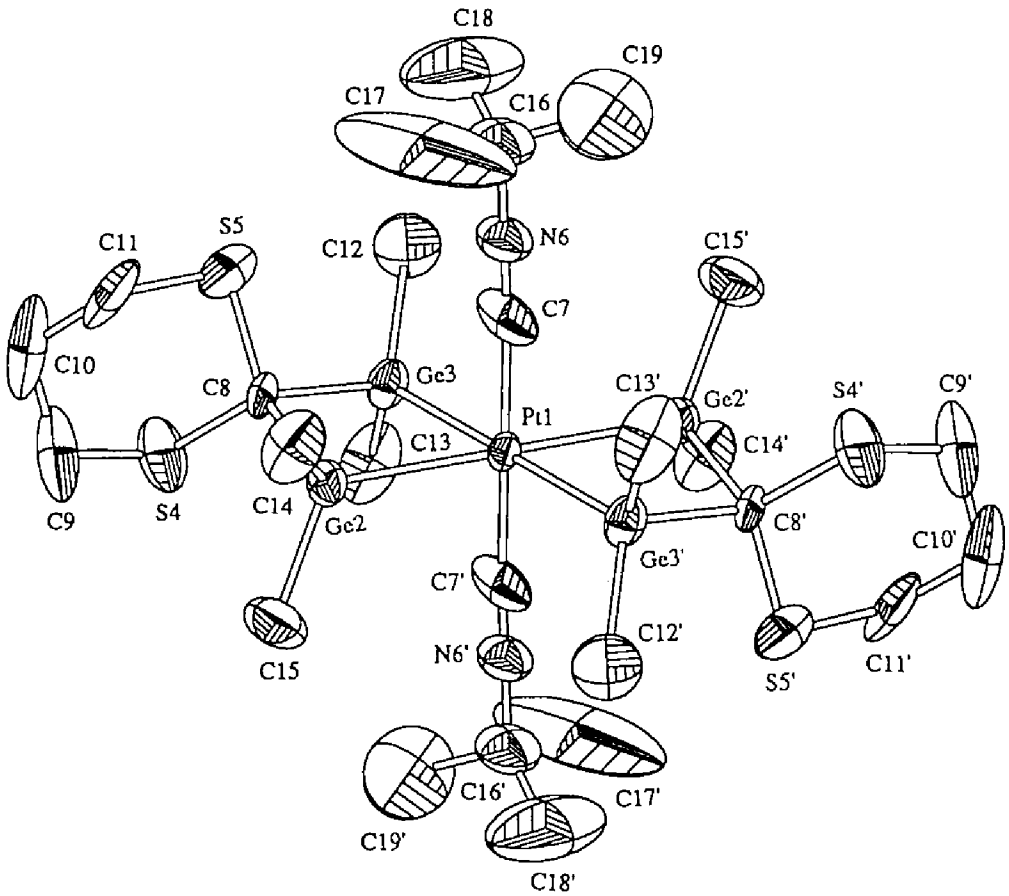


Figure 3. Crystal structure of **9**. The thermal elipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances and angles are follows: Pt(1)–Ge(2) = 2.506(2), Pt(1)–Ge(3) = 2.489(3), Pt(1)–C(7) = 1.98(3), N(6)–C(7) = 1.14(3); Ge(2)–Pt(1)–Ge(3) = 72.7(1), Ge(2)–Pt(1)–Ge(3') = 107.3(1), Ge(2)–Pt(1)–C(7) = 90.7(7), Ge(2)–Pt(1)–C(7') = 89.3(7), Ge(3)–Pt(1)–C(7) = 90.8(7), Ge(3)–Pt(1)–C(7') = 89.2(7), Pt(1)–Ge(2)–C(8) = 94.9(5), Pt(1)–Ge(3)–C(8) = 95.6(6), Ge(2)–C(8)–Ge(3) = 94.5(7).

Experimental Section

General and Materials. All reactions were carried out under a dry or an argon atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian VXR-200. Proton chemical shifts are referenced to internal residual solvent protons: $CDCl_3$, 7.25; C_6D_6, 7.20. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents: $CDCl_3$, 77.0; C_6D_6, 128.0. Silicon chemical shifts are referenced to the signals of tetramethylsilane. Melting point were uncorrected. IR spectra were recorded with a Hitachi 270-30 spectrometer. Complexes $Pt_3(CNBu^t)_6$, $Pt_3(CNAd)_6$[5] and $Pd(CNBu^t)_2$[6] were prepared as previously described. Chlorodimethyl(dimethylphenylsilyl)germane was prepared by chlorodephenylation of dimethylphenyl(dimethylphenylsilyl)germane, which was synthesized by the reaction of dimethylphenylgermyllithium[7] with chlorodimethylphenylsilane, promoted by dry HCl gas in the presence of a catalytic amount of $AlCl_3$ at 0°C.

Reaction of Bis(disilanyl)dithiane with $Pt_3(CNBu^t)_6$. To a benzene (1 mL) solution of $Pt_3(CNBu^t)_6$ (14 mg, 0.017 mmol) and *t*-butyl isocyanide (8.3 mg, 0.1 mmol) was added **1** (25 mg, 0.05 mmol) at room temperature under argon. The mixture was stirred at reflux temperature for 24h, cooled to room temperature, and then subjected to preparative TLC (CH_2Cl_2 : hexane = 60 : 40) to furnish **3** (11.5 mg, 27%). The complex **3** was air and thermally stable.

3: mp 166.0–167.0°C (dec.); ^{1}H NMR ($CDCl_3$) δ 0.46 (s, $^{3}J_{Pt-H}$ = 12.1 Hz, 12 H), 0.53 (s, $^{3}J_{Pt-H}$ = 12.0 Hz, 12 H), 1.46 (s, 18 H), 1.88–2.00 (m, 2 H), 2.52–2.58 (m, 4 H), 7.20–7.30 (m, 6 H), 7.40–7.48 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 1.4 (br), 5.1 ($^{2}J_{Pt-C}$ = 28.3 Hz), 26.2, 28.9, 29.9, 33.5 ($^{2}J_{Pt-C}$ = 103.6 Hz), 58.1 ($^{3}J_{Pt-C}$ = 11.0 Hz), 117.2 (br), 126.8, 127.0, 133.6, 149.0 ($^{2}J_{Pt-C}$ = 20.6 Hz); ^{29}Si NMR ($CDCl_3$) δ -29.6 (br $^{1}J_{Pt-Si}$ = 383 Hz), -30.1 ($^{1}J_{Pt-Si}$ = 461 Hz); IR (KBr) 2900, 2172, 1232, 800 cm^{-1}. Anal. Calcd for $C_{34}H_{58}N_2PtS_2Si_4$: C, 47.13; H, 6.75; N, 3.23. Found: C, 47.01; H, 6.88; N, 3.21.

Reaction of Hexamethyldisilane with $Pt_3(CNAd)_6$. To a benzene (3 mL) solution of $Pt_3(CNAd)_6$ (23 mg, 0.033 mmol) was added hexamethyldisilane (146 mg, 1.0 mmol) at room temperature under argon. After 8h at reflux temperature, evaporation of the solvent followed by washing with pentane afforded spectroscopi-

cally pure **4** (61.5 mg, 93%) as a crystalline solid. **4**: mp 155.0–158.0°C (dec.); ^{1}H NMR (C_6D_6) δ 0.95 (s, $^3J_{Pt-H}$ = 16.3 Hz, 18 H), 1.22 (br, 12 H), 1.62 (br, 6 H), 1.84 (br, 12 H); ^{13}C NMR (C_6D_6) δ 7.7 ($^2J_{Pt-C}$ = 45.9 Hz), 28.9, 35.2, 43.0, 57.9 ($^3J_{Pt-C}$ = 15.6 Hz), 146.4 (br); IR (KBr) 2940, 2144, 822 cm^{-1}. Anal. Calcd for $C_{28}H_{48}N_2PtSi_2$: C, 50.65; H, 7.29; N, 4.22. Found: C, 50.65; H, 7.34; N, 4.25.

2,2-Bis[dimethyl(dimethylphenylsilyl)germyl]-1,3-dithiane (5). To a THF (25 mL) solution of 2-[dimethyl(dimethylphenylsilyl)germyl]-1,3-dithiane, prepared quantitatively from 1,3-dithiane (0.32 g, 2.7 mmol), *n*-butyllithium (2.7 mmol), and chlorodimethyl(dimethylphenylsilyl)germane (0.73 g, 2.7 mmol) in ether, was added *n*-butyllithium (2.7 mmol) at -15°C. The mixture was stirred at -15°C for 15 min. and at 0°C for 45 min., and then treated with chlorodimethyl-(dimethylphenylsilyl)germane (0.73 g, 2.7 mmol) in THF (10 mL). After stirring at room temperature for 3.5 h, saturated aqueous NH_4Cl (20 mL) was added to the solution. Extractive work-up followed by medium-pressure liquid chromatography (hexane / EtOAc = 19 / 1) afforded **5** (0.74g, 47% from 1,3-dithiane). **5**: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 12 H), 0.57 (s, 12 H), 1.74–1.89 (m, 2 H), 2.34–2.44 (m, 4 H), 7.28–7.37 (m, 6 H), 7.45–7.54 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -1.6, -1.1, 24.8, 28.3, 29.2, 127.6, 128.5, 134.1, 139.6; IR (neat) 2968, 1430, 1246, 1108 cm^{-1}. Anal. Calcd for $C_{24}H_{40}Ge_2S_2Si_2$: C, 48.52; H, 6.79. Found: C, 48.30; H, 6.86.

Synthesis of Complex 6. To a benzene (0.25 mL) solution of bis(*t*-butyl isocyanide)palladium(0), prepared from $Pd(C_5H_5)(C_3H_5)$ (21 mg, 0.1 mmol) and *t*-butyl isocyanide (33 mg, 0.4 mmol), was added **5** (65.3 mg, 0.11 mmol) at room temperature under argon. After 10 min., pentane (1 mL) was added to the solution to precipitate colorless crystals of **6**, which was washed twice with 2-propanol (0.5 mL) and dried in vacuo. The complex **6** (49.4mg, 0.083 mmol, 83 %) was thermally stable under nitrogen but gradually decomposed by exposure to the air. **6**: mp 158.5–160°C (dec.); ^{1}H NMR (C_6D_6) δ 0.90 (s, 18 H), 1.09 (s, 12 H), 2.00–2.14 (m, 2 H), 2.67–2.78 (m, 4 H); ^{13}C NMR (C_6D_6) δ 2.1, 28.0, 29.9, 31.0, 35.8, 56.0, 146.6 (br); IR (C_6H_6) 2146 cm^{-1}. Anal. Calcd for $C_{18}H_{36}Ge_2N_2PdS_2$: C, 36.26; H, 6.09; N, 4.70. Found: C, 36.02; H, 6.17; N, 4.49.

Stoichiometric Reaction of the Complex 6 with Phenylacetylene. To a solution of **6** (18.5 mg, 31 μmol) in benzene-d_6 (0.6 mL) was added phenylacetylene (6.3 mg, 62 μmol) at room temperature. The reaction mixture was immediately subjected to preparative TLC (hexane / ether = 19 / 1) to furnish **7** (11.8 mg, 89 %). **7**; mp.

52.0-55.0 °C. ^{1}H NMR ($CDCl_3$) δ 0.58 (s, 6 H), 0.63 (s, 6 H), 2.01–2.14 (m, 2 H), 2.65–2.76 (m, 4 H), 7.06 (s, 1 H), 7.16–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -0.8, -0.6, 25.9, 26.6, 30.1, 126.3, 127.1, 128.4, 142.3, 142.5, 161.3; IR (neat) 2916, 1490, 1424, 1236, 814 cm^{-1}. Anal. Calcd for $C_{16}H_{24}Ge_2S_2$: C, 44.93; H, 5.61. Found: C, 45.14; H, 5.68.

Reaction of 5 with $Pt_3(CNBu^t)_6$. To a benzene (4 mL) solution of $Pt_3(CNBu^t)_6$ (28 mg, 0.034 mmol) and *t*-butyl isocyanide (17 mg, 0.2 mmol) was added **5** (59 mg, 0.1 mmol) at room temperature under argon. The mixture was stirred at reflux temperature for 24h, cooled to room temperature, and then subjected to preparative TLC (CH_2Cl_2 : hexane = 60 : 40) to furnish **8** (29 mg, 30%) and **9** (5.4 mg, 11%). The complex **8** and **9** were air and thermally stable.

8: mp 181.0–182.0°C (dec.); ^{1}H NMR ($CDCl_3$) δ 0.53 (s, $^3J_{Pt-H}$ = 13.5 Hz, 12 H), 0.54 (s, $^3J_{Pt-H}$ = 8.8 Hz, 12 H), 1.48 (s, 18 H), 1.88–2.00 (m, 2 H), 2.46–2.54 (m, 4 H), 7.20–7.30 (m, 6 H), 7.38–7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -0.4 (br), 5.3 ($^2J_{Pt-C}$ = 33.0 Hz), 26.4, 29.5, 30.0, 44.6 ($^2J_{Pt-C}$ = 85.7 Hz), 58.3 ($^3J_{Pt-C}$ = 11.3 Hz), 117.1 (br), 127.0, 127.1, 133.5, 148.3 ($^2J_{Pt-C}$ = 23.5 Hz); ^{29}Si NMR ($CDCl_3$) δ -26.3 ($^1J_{Pt-Si}$ = 515 Hz); IR (KBr) 2904, 2172, 1194, 798 cm^{-1}. Anal. Calcd for $C_{34}H_{58}Ge_2N_2PtS_2Si_2$: C, 42.74; H, 6.12; N, 2.93. Found: C, 42.69; H, 6.19; N, 2.95.

9: mp more than 300°C ; 1H NMR ($CDCl_3$) δ 0.74 (s, $^3J_{Pt-H}$ = 12.1 Hz, 24 H), 1.61 (s, 18 H), 1.92–2.04 (m, 4 H), 2.48–2.56 (m, 8 H). Anal. Calcd for $C_{26}H_{54}Ge_4N_2PtS_4$: C, 30.97; H, 5.40; N, 2.78. Found: C, 31.26; H, 5.41; N, 2.87.

Single Crystal X-ray Analysis of 3. Suitable single crystals of **3** was grown from chloroform–2-propanol at ambient temperature. A crystal of **3** was mounted on a glass fiber using epoxy resin. Data collection were carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 86.375 cm^{-1}). The structures were solved by direct methods and refined full-matrix least-squares procedure against |*F*| with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the refinement. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 1. Final positional parameters are listed in Table 3. Anisotropic thermal parameters are given in Table 4. Intramolecular bond distances are presented in Table 5.

Intramolecular bond angles are presented in Table 6.

Single Crystal X-ray Analysis of 6. Suitable single crystals of **6** was grown from benzene–pentane (1/4) at ambient temperature. A crystal of **6** was coated with silicon grease was mounted in a thin-walled glass capillary under an argon atmosphere. Data collection were carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 96.629 cm^{-1}). The structures were solved by direct methods and refined full-matrix least-squares procedure against |*F*| with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the refinement. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 1. Final positional parameters are listed in Table 7. Anisotropic thermal parameters are given in Table 8. Intramolecular bond distances are presented in Table 9. Intramolecular bond angles are presented in Table 10.

Single Crystal X-ray Analysis of 9. Suitable single crystals of **9** was grown from dichloromethane–2-propanol at ambient temperature. A crystal of **9** was mounted on a glass fiber using epoxy resin. Data collection were carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 121.96 cm^{-1}). The structures were solved by direct methods and refined full-matrix least-squares procedure against |*F*| with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 2. Final positional parameters are listed in Table 11. Anisotropic thermal parameters are given in Table 12. Intramolecular bond distances are presented in Table 13. Intramolecular bond angles are presented in Table 14.

Table 1. Summary of Crystallographic Data for **3** and **6**

compound	**3**	**6**
formula	$C_{34}H_{58}N_2PtS_2Si_4$	$C_{18}H_{36}Ge_2N_2PdS_2$
formula weight	866.4	596.2
crystal system	monoclinic	triclinic
space group	*P21/c* (No. 14)	*P*1 (No. 1)
a, Å	19.298 (8)	8.263 (4)
b, Å	17.196 (8)	10.936 (6)
c, Å	12.552 (6)	15.431 (8)
α, deg		94.57 (4)
β, deg	95.82 (3)	100.06 (4)
γ, deg		102.40 (4)
cell vol, Å^3	4144 (3)	1331 (1)
Z	4	2
ρ(calcd), g cm^{-3}	1.39	1.49
F(000)	1768	600
crystal size, mm	0.40 × 0.40 × 0.20	0.30 × 0.55 × 0.70
μ, cm^{-1}	86.375	96.63
diffractometer	Mac Science MXC3	Mac Science MXC3
monochromator	graphite	graphite
radiation	Cu Kα (λ = 1.54178 Å)	Cu Kα (λ = 1.54178 Å)
temp, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
2θmax, deg	130	130
reflns measured	7683	4939
independent reflns	6671	4454
reflns used	5399	3694
no. of variables	385	448
R, *Rw*	0.103, 0.135	0.067, 0.091
goodness of fit	6.04	1.67
max δ/σ in final cycle	0.53	0.48
residual electron density (min, max) (e/Å^3)	-5.48, 5.19	

Table 2. Summary of Crystallographic Data for **9**

compound	**9**
formula	$C_{26}H_{54}Ge_4N_2PtS_4$
formula weight	1008.5
crystal system	monoclinic
space group	*P*21/a (No. 14)
a, Å	13.061 (6)
b, Å	16.809 (9)
c, Å	9.563 (4)
α, deg	
β, deg	111.38 (3)
γ, deg	
cell vol, Å^3	1955 (2)
Z	2
ρ(calcd), g cm^{-3}	1.713
F(000)	988
crystal size, mm	0.50 × 0.40 × 0.40
μ, cm^{-1}	121.96
diffractometer	Mac Science MXC3
monochromator	graphite
radiation	Cu Kα (λ = 1.54178 Å)
temp, K	293
scan type	$\omega/2\theta$
2θmax, deg	130
reflns measured	3610
independent reflns	3204
reflns used	2860
no. of variables	196
R, *Rw*	0.080, 0.093
goodness of fit	6.28
max δ/σ in final cycle	0.42
residual electron density (min, max) (e/Å^3)	-4.98, 2.86

Table 3. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$) with Esd's in Parentheses for **3**

atom	x/a	y/b	z/c	U(iso)
Pt1	0.23681(4)	-0.00217(4)	0.17596(6)	0.036
Si2	0.2474(3)	0.0025(3)	0.3754(5)	0.048
Si3	0.1561(3)	0.0932(3)	0.2409(5)	0.047
Si4	0.3292(3)	-0.0988(4)	0.1501(6)	0.055
Si5	0.1952(3)	0.0219(4)	-0.0138(5)	0.051
S 6	0.1687(4)	0.1445(3)	0.4800(5)	0.070
S 7	0.0888(3)	0.0026(3)	0.4067(6)	0.066
N 8	0.1319(9)	-0.1367(9)	0.1819(12)	0.045
N 9	0.3473(9)	0.1251(11)	0.1615(17)	0.064
C 10	0.1695(9)	-0.0855(13)	0.1798(14)	0.044
C 11	0.30696	0.07420	0.16800	0.048
C 12	0.1633(9)	0.0616(11)	0.3904(16)	0.048
C 13	0.1730(17)	0.0980(18)	0.6111(19)	0.092
C 14	0.1059(16)	0.0476(22)	0.6222(21)	0.091
C 15	0.1007(17)	-0.0258(20)	0.5473(26)	0.088
C 16	0.2445(15)	-0.0937(14)	0.4464(19)	0.088
C 17	0.3242(12)	0.0583(17)	0.4333(20)	0.074
C 18	0.0620(12)	0.0918(17)	0.1815(22)	0.083
C 19	0.1870(16)	0.1971(13)	0.2359(21)	0.082
C 20	0.2914(15)	-0.1967(17)	0.1055(32)	0.115
C 21	0.3942(13)	-0.0719(17)	0.0530(19)	0.078
C 22	0.1103(16)	-0.0314(21)	-0.0575(23)	0.092
C 23	0.1754(16)	0.1292(15)	-0.0429(20)	0.084
C 24	0.3901(12)	-0.1160(13)	0.2780(19)	0.068
C 25	0.3817(17)	-0.1829(20)	0.3434(31)	0.127
C 26	0.425(2)	-0.192(4)	0.443(5)	0.168
C 27	0.472(3)	-0.142(5)	0.457(4)	0.189
C 28	0.4910(17)	-0.0721(29)	0.3951(30)	0.128
C 29	0.4449(13)	-0.0626(19)	0.3039(22)	0.084
C 30	0.2573(15)	-0.0045(11)	-0.1169(18)	0.057
C 31	0.2510(17)	-0.0801(16)	-0.1685(21)	0.088
C 32	0.301(2)	-0.099(2)	-0.245(2)	0.098
C 33	0.350(2)	-0.043(3)	-0.269(2)	0.108
C 34	0.3527(19)	0.0304(25)	-0.2208(35)	0.115
C 35	0.3071(14)	0.0467(16)	-0.1437(21)	0.075
C 36	0.0790(12)	-0.1985(13)	0.1881(20)	0.067
C 37	0.0099(18)	-0.1653(22)	0.1812(53)	0.196
C 38	0.099(2)	-0.241(3)	0.292(4)	0.210
C 39	0.079(3)	-0.248(2)	0.088(4)	0.205
C 40	0.3999(14)	0.1832(16)	0.1488(23)	0.079
C 41	0.463(2)	0.153(3)	0.132(8)	0.362
C 42	0.377(3)	0.229(4)	0.054(5)	0.291
C 43	0.408(4)	0.234(5)	0.237(6)	0.327

$T=\exp[-2\pi^2 U]$, U=U(iso) or [U(11)+U(22)+U(33)]/3

Table 4. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **3**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Pt1	0.0325(6)	0.0430(6)	0.0323(6)	0.0023(3)	0.0031(4)	0.0007(3)
Si2	0.036(3)	0.067(4)	0.041(3)	0.009(2)	0.004(2)	-0.003(3)
Si3	0.045(3)	0.053(3)	0.043(3)	0.016(2)	0.006(2)	0.001(3)
Si4	0.043(3)	0.055(3)	0.067(4)	0.010(3)	0.014(3)	-0.003(3)
Si5	0.055(3)	0.060(3)	0.038(3)	-0.004(3)	-0.005(3)	0.009(3)
S 6	0.097(5)	0.058(3)	0.055(4)	0.006(3)	0.013(3)	-0.013(3)
S 7	0.042(3)	0.080(4)	0.074(4)	-0.001(2)	0.013(3)	0.004(3)
N 8	0.06(1)	0.04(1)	0.04(1)	-0.01(1)	0.00(1)	-0.01(1)
N 9	0.05(1)	0.06(1)	0.08(1)	-0.02(1)	0.01(1)	0.00(1)
C 10	0.04(1)	0.07(1)	0.02(1)	0.00(1)	-0.01(1)	0.01(1)
C 11	0.05(1)	0.05(1)	0.04(1)	0.00(1)	0.00(1)	0.01(1)
C 12	0.04(1)	0.06(1)	0.05(1)	0.01(1)	0.00(1)	-0.01(1)
C 13	0.14(3)	0.10(2)	0.04(1)	0.01(2)	0.01(2)	-0.01(1)
C 14	0.09(2)	0.14(3)	0.05(2)	0.02(2)	0.03(1)	0.00(2)
C 15	0.10(2)	0.10(2)	0.07(2)	0.00(2)	0.02(2)	0.02(2)
C 16	0.13(2)	0.07(2)	0.06(1)	0.05(2)	0.04(2)	0.04(1)
C 17	0.05(1)	0.11(2)	0.06(2)	0.01(1)	0.01(1)	-0.02(1)
C 18	0.05(1)	0.12(2)	0.08(2)	0.03(1)	0.00(1)	0.00(2)
C 19	0.13(2)	0.05(1)	0.07(2)	0.01(1)	0.03(2)	-0.01(1)
C 20	0.08(2)	0.07(2)	0.19(4)	0.00(1)	0.02(2)	-0.06(2)
C 21	0.07(2)	0.11(2)	0.05(1)	0.04(1)	0.03(1)	0.01(1)
C 22	0.08(2)	0.14(2)	0.06(2)	-0.03(2)	-0.02(1)	0.02(2)
C 23	0.13(2)	0.06(2)	0.06(2)	0.02(2)	0.01(2)	0.03(1)
C 24	0.07(2)	0.07(1)	0.07(2)	0.03(1)	0.03(1)	0.02(1)
C 25	0.10(2)	0.12(3)	0.15(3)	0.08(2)	0.07(2)	0.08(2)
C 26	0.13(4)	0.23(6)	0.14(4)	0.13(4)	0.09(4)	0.10(4)
C 27	0.15(5)	0.34(10)	0.07(2)	0.17(6)	0.04(3)	0.08(5)
C 28	0.08(2)	0.21(5)	0.09(3)	0.05(3)	-0.02(2)	-0.01(3)
C 29	0.05(1)	0.13(2)	0.07(2)	0.02(2)	-0.01(1)	-0.03(2)
C 30	0.08(2)	0.06(1)	0.03(1)	-0.01(1)	0.00(1)	0.00(1)
C 31	0.13(3)	0.08(2)	0.06(2)	0.01(2)	-0.02(2)	-0.03(1)
C 32	0.14(3)	0.11(2)	0.05(2)	0.01(2)	-0.01(2)	-0.01(2)
C 33	0.13(3)	0.15(4)	0.04(2)	0.05(3)	0.00(2)	-0.02(2)
C 34	0.09(3)	0.12(3)	0.13(3)	0.01(2)	0.03(2)	0.02(3)
C 35	0.08(2)	0.08(2)	0.06(2)	0.00(1)	0.02(1)	0.01(1)
C 36	0.06(1)	0.06(1)	0.08(2)	-0.03(1)	0.02(1)	0.00(1)
C 37	0.07(2)	0.10(3)	0.42(9)	-0.02(2)	0.05(3)	-0.01(4)
C 38	0.18(4)	0.21(5)	0.24(5)	-0.13(4)	-0.09(4)	0.19(4)
C 39	0.29(6)	0.14(4)	0.18(4)	-0.15(4)	0.10(4)	-0.10(3)
C 40	0.07(2)	0.08(2)	0.08(2)	-0.03(1)	0.01(1)	0.00(2)
C 41	0.12(4)	0.11(4)	0.84(17)	-0.02(3)	0.22(7)	0.04(6)
C 42	0.24(6)	0.35(8)	0.28(7)	-0.23(6)	-0.14(5)	0.25(7)
C 43	0.4(1)	0.3(1)	0.3(1)	-0.3(1)	0.1(1)	-0.2(1)

Table 5. Intramolecular Distances (Å) with Esd's in Parentheses for **3**

atom	atom	distance	atom	atom	distance
Pt1	- Si2	2.493(7)	Pt1	- Si3	2.457(6)
Pt1	- Si4	2.482(7)	Pt1	- Si5	2.470(7)
Pt1	- C 10	1.94(3)	Pt1	- C 11	1.896(1)
Si2	- C 12	1.94(2)	Si2	- C 16	1.88(3)
Si2	- C 17	1.85(3)	Si3	- C 12	1.95(3)
Si3	- C 18	1.89(3)	Si3	- C 19	1.89(3)
Si4	- C 24	1.91(3)	Si4	- C 21	1.89(3)
Si4	- C 20	1.90(4)	Si5	- C 30	1.90(3)
Si5	- C 23	1.91(3)	Si5	- C 22	1.91(4)
S 6	- C 12	1.81(3)	S 6	- C 13	1.82(3)
S 7	- C 12	1.79(2)	S 7	- C 15	1.82(4)
C 13	- C 14	1.58(5)	C 15	- C 14	1.57(5)
C 10	- N 8	1.14(3)	C 11	- N 9	1.179(19)
N 8	- C 36	1.48(3)	N 9	- C 40	1.45(4)
C 24	- C 25	1.43(5)	C 26	- C 25	1.44(7)
C 26	- C 27	1.25(9)	C 28	- C 27	1.50(9)
C 29	- C 28	1.39(5)	C 24	- C 29	1.41(4)
C 30	- C 31	1.45(4)	C 30	- C 35	1.37(4)
C 31	- C 32	1.46(5)	C 33	- C 32	1.40(6)
C 33	- C 34	1.39(7)	C 35	- C 34	1.40(5)
C 36	- C 37	1.45(5)	C 36	- C 38	1.51(6)
C 36	- C 39	1.52(6)	C 40	- C 42	1.46(8)
C 40	- C 41	1.36(6)	C 40	- C 43	1.41(9)

Table 6. Intramolecular Angles (deg) with Esd's in Parentheses for **3**

atom	atom	atom	angle	atom	atom	atom	angle
Si2	- Pt1	- Si3	68.6(2)	Si2	- Pt1	- Si4	99.5(3)
Si2	- Pt1	- Si5	161.6(3)	Si2	- Pt1	- C 10	89.2(6)
Si2	- Pt1	- C 11	92.5(2)	Si3	- Pt1	- Si4	168.0(3)
Si3	- Pt1	- Si5	93.0(3)	Si3	- Pt1	- C 10	92.1(6)
Si3	- Pt1	- C 11	92.0(2)	Si4	- Pt1	- Si5	98.8(3)
Si4	- Pt1	- C 10	90.0(7)	Si4	- Pt1	- C 11	86.0(2)
Si5	- Pt1	- C 10	89.7(6)	Si5	- Pt1	- C 11	89.8(2)
C 10	- Pt1	- C 11	175.9(6)	Pt1	- Si2	- C 12	97.4(7)
Pt1	- Si2	- C 16	116.3(8)	Pt1	- Si2	- C 17	113.1(9)
C 12	- Si2	- C 16	110.4(11)	C 12	- Si2	- C 17	109.6(11)
C 16	- Si2	- C 17	109.4(13)	C 12	- S 6	- C 13	102.1(12)
C 12	- S 7	- C 15	103.8(13)	Pt1	- Si3	- C 12	98.5(7)
Pt1	- Si3	- C 18	118.4(10)	Pt1	- Si3	- C 19	114.1(10)
C 12	- Si3	- C 18	110.4(11)	C 12	- Si3	- C 19	107.7(11)
C 18	- Si3	- C 19	107.0(13)	Pt1	- Si4	- C 24	112.5(8)
Pt1	- Si4	- C 21	116.9(9)	Pt1	- Si4	- C 20	111.9(10)
C 24	- Si4	- C 21	100.7(11)	C 24	- Si4	- C 20	107.2(14)
C 21	- Si4	- C 20	106.7(14)	Pt1	- Si5	- C 30	116.8(9)
Pt1	- Si5	- C 23	112.6(8)	Pt1	- Si5	- C 22	112.5(10)

C 30	- Si5	- C 23	103.1(11)	C 30	- Si5	- C 22	105.7(13)
C 23	- Si5	- C 22	105.0(14)	Pt1	- C 10	- N 8	177.4(18)
Pt1	- C 11	- N 9	175.7(10)	C 10	- N 8	- C 36	175.3(20)
C 11	- N 9	- C 40	175.4(21)	Si2	- C 12	- S 6	118.4(11)
Si2	- C 12	- S 7	113.8(11)	Si2	- C 12	- Si3	91.8(9)
S 6	- C 12	- S 7	111.8(11)	S 6	- C 12	- Si3	111.9(11)
S 7	- C 12	- Si3	106.8(10)	S 6	- C 13	- C 14	111.0(19)
S 7	- C 15	- C 14	111.0(22)	C 15	- C 14	- C 13	113.0(24)
Si4	- C 24	- C 25	120.6(20)	Si4	- C 24	- C 29	118.3(19)
C 24	- C 25	- C 26	119.7(35)	C 25	- C 26	- C 27	113.6(53)
C 26	- C 27	- C 28	133.4(50)	C 29	- C 28	- C 27	110.8(36)
C 24	- C 29	- C 28	121.0(31)	C 29	- C 24	- C 25	121.1(25)
Si5	- C 30	- C 31	119.1(20)	Si5	- C 30	- C 35	121.3(17)
C 30	- C 31	- C 32	117.2(27)	C 33	- C 32	- C 31	119.4(31)
C 32	- C 33	- C 34	122.0(34)	C 33	- C 34	- C 35	118.4(35)
C 30	- C 35	- C 34	123.2(28)	C 31	- C 30	- C 35	119.6(25)
N 8	- C 36	- C 37	110.5(22)	N 8	- C 36	- C 38	105.7(24)
N 8	- C 36	- C 39	107.8(25)	N 9	- C 40	- C 41	113.7(29)
N 9	- C 40	- C 42	107.4(31)	N 9	- C 40	- C 43	111.7(39)
C 37	- C 36	- C 38	113.5(34)	C 37	- C 36	- C 39	104.2(35)
C 38	- C 36	- C 39	115.1(30)	C 41	- C 40	- C 43	108.8(53)
C 42	- C 40	- C 41	107.0(50)	C 42	- C 40	- C 43	107.9(45)

Table 7. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å²) with Esd's in Parentheses for **6**

atom	x/a	y/b	z/c	U(iso)
Pd1A	0.8656(3)	0.7422(2)	0.5637(1)	0.054
Pd1B	0.84500	0.60900	0.14600	0.057
Ge2A	1.0953(7)	0.7556(5)	0.6866(3)	0.053
Ge2B	0.6128(7)	0.5935(4)	0.0203(3)	0.054
Ge3A	1.0682(7)	0.9405(5)	0.5757(3)	0.060
Ge3B	0.6456(7)	0.4096(5)	0.1309(4)	0.063
S 4A	1.4236(15)	0.8879(12)	0.6111(8)	0.070
S 4B	0.3788(15)	0.3110(11)	-0.0496(8)	0.072
S 5A	1.3362(17)	1.0421(10)	0.7568(7)	0.069
S 5B	0.2857(16)	0.4654(14)	0.0929(9)	0.083
N 6A	0.679(5)	0.476(3)	0.609(2)	0.066
N 6B	1.027(4)	0.877(3)	0.112(2)	0.059
N 7A	0.653(5)	0.819(4)	0.397(2)	0.069
N 7B	1.050(5)	0.518(3)	0.314(2)	0.072
C 8A	0.738(6)	0.562(4)	0.587(4)	0.105
C 8B	0.968(3)	0.777(2)	0.123(1)	0.039
C 9A	0.720(5)	0.803(3)	0.454(2)	0.058
C 9B	0.987(6)	0.575(3)	0.255(3)	0.071
C 10A	1.264(3)	0.918(3)	0.672(2)	0.053
C 10B	0.456(4)	0.442(2)	0.044(2)	0.051
C 11A	1.211(6)	0.612(3)	0.697(3)	0.079
C 11B	0.679(7)	0.552(8)	-0.086(3)	0.166
C 12A	1.032(5)	0.784(3)	0.807(3)	0.077
C 12B	0.519(6)	0.742(5)	0.024(4)	0.110

C 13A	1.140(5)	0.991(4)	0.472(3)	0.089
C 13B	0.726(7)	0.270(5)	0.098(3)	0.086
C 14A	0.990(6)	1.083(5)	0.643(4)	0.108
C 14B	0.550(8)	0.364(9)	0.246(4)	0.195
C 15A	1.574(3)	0.857(2)	0.706(2)	0.053
C 15B	0.228(6)	0.386(5)	-0.113(3)	0.083
C 16A	1.628(5)	0.966(4)	0.787(3)	0.074
C 16B	0.074(7)	0.412(6)	-0.068(4)	0.129
C 17A	1.496(6)	0.993(4)	0.834(2)	0.074
C 17B	0.130(9)	0.525(6)	0.015(5)	0.155
C 18A	0.625(4)	0.354(3)	0.635(2)	0.052
C 18B	1.116(6)	1.005(4)	0.086(3)	0.071
C 19A	0.743(8)	0.330(5)	0.702(4)	0.112
C 19B	0.980(5)	1.025(4)	-0.004(3)	0.080
C 20A	0.587(6)	0.258(3)	0.544(3)	0.081
C 20B	1.275(6)	0.988(5)	0.062(4)	0.104
C 21A	0.441(7)	0.346(6)	0.661(4)	0.116
C 21B	1.108(11)	1.105(5)	0.153(4)	0.152
C 22A	0.581(6)	0.888(4)	0.323(2)	0.072
C 22B	1.114(6)	0.470(5)	0.391(3)	0.080
C 23A	0.690(8)	0.890(8)	0.263(4)	0.145
C 23B	1.122(7)	0.328(4)	0.340(3)	0.097
C 24A	0.399(12)	0.801(12)	0.289(9)	0.261
C 24B	1.302(5)	0.546(4)	0.429(2)	0.077
C 25A	0.518(11)	0.988(6)	0.352(3)	0.175
C 25B	0.991(8)	0.455(6)	0.458(3)	0.121

T=exp[-2π²U], U=U(iso) or [U(11)+U(22)+U(33)]/3

Table 8. Anisotropic Thermal Parameters (Å²) with Esd's in Parentheses for **6**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	U11	U22	U33	U12	U13	U23
Pd1A	0.064(2)	0.037(1)	0.049(2)	0.005(1)	-0.009(1)	0.017(1)
Pd1B	0.057(2)	0.053(2)	0.050(2)	0.017(1)	0.004(1)	0.015(1)
Ge2A	0.056(3)	0.048(2)	0.045(2)	0.017(2)	-0.002(2)	0.018(2)
Ge2B	0.069(3)	0.040(2)	0.042(2)	0.015(2)	0.007(2)	0.016(2)
Ge3B	0.060(3)	0.047(3)	0.071(3)	0.007(2)	-0.007(2)	0.032(2)
S 4B	0.078(7)	0.058(6)	0.066(7)	0.021(5)	0.009(5)	0.001(5)
S 4A	0.064(6)	0.074(7)	0.060(6)	0.020(5)	0.017(4)	0.019(5)
S 5B	0.074(7)	0.097(8)	0.061(6)	0.044(6)	0.021(5)	0.028(6)
S 5A	0.090(8)	0.043(5)	0.059(6)	0.012(5)	-0.012(5)	0.003(4)
N 6A	0.09(2)	0.05(2)	0.05(1)	0.03(2)	0.02(1)	0.02(1)
N 6B	0.06(1)	0.05(2)	0.06(2)	0.01(1)	0.02(1)	-0.01(1)
N 7A	0.07(2)	0.07(2)	0.05(2)	0.01(2)	-0.02(2)	0.02(1)
N 7B	0.08(2)	0.08(2)	0.04(1)	0.04(2)	0.01(1)	0.01(1)
C 8A	0.10(3)	0.04(2)	0.15(4)	-0.04(2)	-0.03(3)	0.03(2)
C 8B	0.05(1)	0.03(1)	0.03(1)	0.02(1)	0.01(1)	0.01(1)
C 9A	0.05(2)	0.06(2)	0.05(2)	0.02(1)	-0.01(1)	0.01(1)
C 9B	0.09(2)	0.04(1)	0.07(2)	0.03(1)	0.02(2)	0.02(1)
C 10A	0.03(1)	0.08(2)	0.04(1)	0.04(1)	0.01(1)	0.00(1)

C 10B	0.08(2)	0.02(1)	0.05(1)	-0.01(1)	-0.02(1)	0.02(1)
C 11A	0.13(3)	0.02(1)	0.08(2)	0.01(1)	-0.02(2)	0.02(1)
C 11B	0.10(4)	0.31(8)	0.05(2)	0.09(5)	0.04(2)	0.07(3)
C 12A	0.09(2)	0.06(2)	0.07(2)	-0.01(2)	0.04(2)	0.02(1)
C 12B	0.08(3)	0.12(4)	0.11(4)	0.07(3)	-0.02(2)	0.02(3)
C 13A	0.06(2)	0.12(3)	0.08(3)	-0.03(2)	0.00(2)	0.07(2)
C 13B	0.09(3)	0.06(2)	0.08(3)	0.03(2)	-0.02(2)	0.01(2)
C 14A	0.07(2)	0.07(2)	0.16(5)	0.03(2)	0.01(3)	0.02(3)
C 14B	0.12(4)	0.34(10)	0.09(3)	0.08(5)	0.05(3)	0.13(5)
C 15A	0.05(1)	0.04(1)	0.06(1)	0.04(1)	0.01(1)	0.01(1)
C 15B	0.08(3)	0.08(3)	0.07(3)	0.01(2)	-0.02(2)	-0.02(2)
C 16A	0.07(2)	0.07(2)	0.07(2)	0.02(2)	-0.03(2)	0.02(2)
C 16B	0.09(3)	0.15(5)	0.12(4)	0.07(3)	0.06(3)	0.04(3)
C 17A	0.11(3)	0.06(2)	0.03(1)	0.04(2)	-0.01(2)	0.00(1)
C 17B	0.17(5)	0.12(4)	0.15(5)	0.11(4)	-0.01(4)	0.00(3)
C 18A	0.05(1)	0.03(1)	0.06(2)	0.00(1)	0.00(1)	-0.01(1)
C 18B	0.09(3)	0.05(2)	0.06(2)	0.02(2)	-0.01(2)	0.03(1)
C 19A	0.13(4)	0.06(3)	0.13(4)	0.02(3)	-0.05(3)	0.00(2)
C 19B	0.07(2)	0.09(3)	0.07(2)	0.03(2)	0.01(2)	0.03(2)
C 20A	0.10(3)	0.03(1)	0.09(3)	-0.01(2)	0.00(2)	-0.01(2)
C 20B	0.07(2)	0.09(3)	0.14(4)	0.02(2)	0.05(2)	0.08(3)
C 21A	0.08(3)	0.12(4)	0.12(4)	0.04(3)	0.04(3)	0.09(3)
C 21B	0.26(8)	0.10(4)	0.06(2)	0.08(4)	-0.04(3)	0.00(2)
C 22A	0.11(3)	0.06(2)	0.03(1)	0.05(2)	0.02(1)	0.03(1)
C 22B	0.08(2)	0.09(3)	0.06(2)	0.02(2)	-0.01(2)	0.00(2)
C 23A	0.08(3)	0.25(7)	0.07(3)	0.05(3)	0.06(2)	0.05(3)
C 23B	0.13(3)	0.05(2)	0.09(3)	0.03(2)	0.00(2)	0.00(2)
C 24A	0.12(6)	0.31(13)	0.31(13)	-0.08(6)	-0.08(7)	0.17(11)
C 24B	0.07(2)	0.10(2)	0.05(1)	0.00(2)	-0.03(1)	0.03(2)
C 25A	0.3(1)	0.1(0)	0.1(0)	0.1(1)	0.0(0)	0.0(0)
C 25B	0.12(4)	0.18(4)	0.04(2)	0.02(3)	0.05(2)	0.04(2)

Table 9. Intramolecular Distances (Å) with Esd's in Parentheses for **6**

atom	atom	distance	atom	atom	distance
Pd1A	- Ge2A	2.409(6)	Pd1A	- Ge3A	2.410(6)
Pd1B	- Ge2B	2.446(5)	Pd1B	- Ge3B	2.401(6)
Pd1A	- C 9A	2.13(4)	Pd1A	- C 8A	2.11(5)
Pd1B	- C 8B	1.99(3)	Pd1B	- C 9B	1.98(5)
Ge2A	- C 10A	2.06(4)	Ge2A	- C 11A	2.01(4)
Ge2A	- C 12A	2.04(4)	Ge2B	- C 12B	1.95(6)
Ge2B	- C 11B	1.87(5)	Ge2B	- C 10B	1.98(3)
Ge3B	- C 13B	1.86(6)	Ge3B	- C 10B	1.98(4)
Ge3B	- C 14B	2.12(7)	Ge3A	- C 10A	2.07(3)
Ge3A	- C 13A	1.88(5)	Ge3A	- C 14A	2.09(6)
S 4B	- C 15B	1.83(6)	S 4B	- C 10B	1.88(3)
S 4A	- C 10A	1.82(4)	S 4A	- C 15A	1.84(4)
S 5B	- C 17B	1.86(8)	S 5B	- C 10B	1.76(4)
S 5A	- C 10A	1.73(4)	S 5A	- C 17A	1.81(5)
N 6A	- C 18A	1.43(5)	N 6A	- C 8A	1.08(6)
N 7B	- C 22B	1.39(6)	N 7B	- C 9B	1.25(6)
C 18A	- C 20A	1.62(6)	C 18A	- C 21A	1.63(7)
C 18A	- C 19A	1.38(8)	C 9A	- N 7A	1.01(6)
N 6B	- C 18B	1.55(6)	N 6B	- C 8B	1.14(5)
C 18B	- C 19B	1.68(7)	C 18B	- C 20B	1.46(7)

C 18B	- C 21B	1.47(7)	N 7A	- C 22A	1.52(6)
C 22B	- C 25B	1.57(8)	C 22B	- C 24B	1.58(7)
C 15A	- C 16A	1.59(5)	C 15B	- C 16B	1.61(8)
C 22A	- C 23A	1.41(8)	C 22A	- C 24A	1.57(11)
C 22A	- C 25A	1.38(8)	C 7B	- C 16B	1.65(9)
C 17A	- C 16A	1.48(6)			

Table 10. Intramolecular Angles (deg) with Esd's in Parentheses for **6**

atom	atom	atom	angle	atom	atom	atom	angle
Ge2B	- Pd1B	- Ge3B	69.6(2)	Ge2B	- Pd1B	- C 8B	93.3(7)
Ge2B	- Pd1B	- C 9B	162.5(12)	Ge3B	- Pd1B	- C 8B	162.6(7)
Ge3B	- Pd1B	- C 9B	93.2(12)	C 8B	- Pd1B	- C 9B	104.0(14)
Ge2A	- Pd1A	- Ge3A	70.2(2)	Ge2A	- Pd1A	- C 9A	157.3(10)
Ge2A	- Pd1A	- C 8A	92.8(16)	Ge3A	- Pd1A	- C 9A	87.1(10)
Ge3A	- Pd1A	- C 8A	163.0(16)	C 9A	- Pd1A	- C 8A	109.9(18)
Pd1A	- Ge2A	- C 10A	102.4(9)	Pd1A	- Ge2A	- C 11A	119.2(12)
Pd1A	- Ge2A	- C 12A	113.5(12)	C 10A	- Ge2A	- C 11A	110.2(15)
C 10A	- Ge2A	- C 12A	106.8(14)	C 11A	- Ge2A	- C 12A	104.2(16)
Pd1B	- Ge2B	- C 12B	111.7(16)	Pd1B	- Ge2B	- C 11B	110.3(17)
Pd1B	- Ge2B	- C 10B	98.9(10)	C 12B	- Ge2B	- C 11B	114.8(28)
C 12B	- Ge2B	- C 10B	112.5(18)	C 11B	- Ge2B	- C 10B	107.5(26)
Pd1B	- Ge3B	- C 13B	115.0(17)	Pd1B	- Ge3B	- C 10B	100.2(8)
Pd1B	- Ge3B	- C 14B	115.8(24)	C 13B	- Ge3B	- C 14B	103.5(29)
C 13B	- Ge3B	- C 10B	115.7(18)	C 14B	- Ge3B	- C 10B	106.9(21)
Pd1A	- Ge3A	- C 13A	118.1(14)	Pd1A	- Ge3A	- C 14A	110.2(14)
Pd1A	- Ge3A	- C 10A	101.9(10)	C 14A	- Ge3A	- C 13A	111.7(21)
C 14A	- Ge3A	- C 10A	99.9(19)	C 10A	- Ge3A	- C 13A	113.1(15)
C 15B	- S 4B	- C 10B	95.3(19)	C 10A	- S 4A	- C 15A	97.3(14)
C 17B	- S 5B	- C 10B	111.8(25)	C 10A	- S 5A	- C 17A	104.7(17)
Ge2A	- C 10A	- Ge3A	84.3(12)	Ge2A	- C 10A	- S 4A	113.2(17)
Ge2A	- C 10A	- S 5A	121.7(17)	Ge3A	- C 10A	- S 4A	104.2(15)
Ge3A	- C 10A	- S 5A	114.2(17)	S 4A	- C 10A	- S 5A	114.1(17)
C 18A	- N 6A	- C 8A	169.8(47)	C 22B	- N 7B	- C 9B	169.9(41)
N 6A	- C 18A	- C 20A	104.9(29)	N 6A	- C 18A	- C 21A	107.1(34)
N 6A	- C 18A	- C 19A	111.1(35)	C 20A	- C 18A	- C 21A	104.6(35)
C 20A	- C 18A	- C 19A	114.8(36)	C 21A	- C 18A	- C 19A	113.7(41)
Pd1A	- C 9A	- N 7A	170.2(38)	C 18B	- N 6B	- C 8B	172.0(35)
N 6B	- C 18B	- C 19B	103.5(31)	N 6B	- C 18B	- C 20B	107.1(35)
N 6B	- C 18B	- C 21B	107.6(38)	C 19B	- C 18B	- C 20B	111.1(37)
C 19B	- C 18B	- C 21B	103.1(40)	C 20B	- C 18B	- C 21B	122.8(49)
Pd1B	- C 8B	- N 6B	174.2(26)	C 9A	- N 7A	- C 22A	160.2(44)
N 7B	- C 22B	- C 25B	113.1(42)	N 7B	- C 22B	- C 24B	109.1(38)
C 25B	- C 22B	- C 24B	116.4(37)	Pd1B	- C 9B	- N 7B	161.8(33)
Pd1A	- C 8A	- N 6A	171.3(49)	S 4A	- C 15A	- C 16A	114.7(22)
S 4B	- C 15B	- C 16B	117.5(37)	N 7A	- C 22A	- C 23A	104.5(43)
N 7A	- C 22A	- C 24A	102.0(54)	N 7A	- C 22A	- C 25A	114.9(34)
C 23A	- C 22A	- C 24A	114.5(57)	C 23A	- C 22A	- C 25A	125.7(53)
C 24A	- C 22A	- C 25A	92.8(60)	S 5B	- C 17B	- C 16B	101.4(39)
C 15B	- C 16B	- C 17B	114.5(47)	S 5A	- C 17A	- C 16A	109.6(26)
C 15A	- C 16A	- C 17A	118.0(31)	Ge2B	- C 10B	- Ge3B	88.5(14)
Ge2B	- C 10B	- S 4B	115.5(17)	Ge2B	- C 10B	- S 5B	117.3(15)
Ge3B	- C 10B	- S 4B	111.1(15)	Ge3B	- C 10B	- S 5B	113.2(17)
S 4B	- C 10B	- S 5B	109.7(18)				

Table 11. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$) with Esd's in Parentheses for **9**

atom	x/a	y/b	z/c	U(iso)
Pt1	1.00000	0.00000	1.00000	0.028
Ge2	1.18268(16)	-0.00472(13)	0.96992(22)	0.042
Ge3	1.12346(16)	0.09540(13)	1.18382(23)	0.041
S 4	1.3418(5)	0.1461(3)	1.1334(9)	0.083
S 5	1.3399(5)	0.0022(4)	1.3180(6)	0.065
N 6	1.0774(14)	-0.1347(10)	1.2402(19)	0.060
C 7	1.0459(18)	-0.0868(12)	1.1508(26)	0.074
C 8	1.2622(13)	0.0592(12)	1.1571(19)	0.042
C 9	1.460(2)	0.098(2)	1.116(4)	0.115
C 10	1.5258(19)	0.0470(20)	1.2534(42)	0.113
C 11	1.4596(18)	-0.0235(18)	1.2778(31)	0.081
C 12	1.139(2)	0.082(2)	1.395(3)	0.094
C 13	1.103(2)	0.211(1)	1.137(4)	0.085
C 14	1.244(2)	-0.109(2)	0.962(3)	0.078
C 15	1.192(2)	0.057(2)	0.798(3)	0.090
C 16	1.116(2)	-0.197(2)	1.348(3)	0.079
C 17	1.201(7)	-0.239(4)	1.313(8)	0.420
C 18	1.168(6)	-0.163(3)	1.494(5)	0.186
C 19	1.023(5)	-0.245(3)	1.344(8)	0.191
H 9A	1.50683	0.13762	1.09731	0.3(2)
H 9B	1.43383	0.06292	1.03171	0.01(4)
H 10A	1.54428	0.08111	1.33973	0.08(8)
H 10B	1.59228	0.02841	1.24363	0.07(7)
H 11A	1.43626	-0.05503	1.18778	0.1(1)
H 11B	1.50706	-0.05503	1.35948	0.06(6)
H 12A	1.18702	0.11867	1.46604	0.3(2)
H 12B	1.16682	0.02917	1.42554	0.2(2)
H 12C	1.06752	0.08657	1.39984	0.06(6)
H 13A	1.15015	0.24781	1.20752	0.09(9)
H 13B	1.02845	0.22411	1.12532	0.2(2)
H 13C	1.11165	0.21941	1.04252	0.2(2)
H 14A	1.31386	-0.11051	0.95043	0.09(9)
H 14B	1.19196	-0.13701	0.87903	0.09(8)
H 14C	1.25146	-0.13581	1.05353	0.09(9)
H 15A	1.26237	0.05490	0.78682	0.06(6)
H 15B	1.17597	0.11130	0.81102	0.08(8)
H 15C	1.13777	0.03650	0.70792	0.1(1)
H 17A	1.22717	-0.28096	1.38551	0.6(8)
H 17B	1.25927	-0.20206	1.32181	0.1(1)
H 17C	1.17297	-0.25996	1.21311	0.2(2)
H 18A	1.19411	-0.20560	1.56633	0.3(3)
H 18B	1.11521	-0.13150	1.51693	0.1(1)
H 18C	1.22821	-0.13040	1.49513	0.1(1)
H 19A	1.04950	-0.28760	1.41604	0.1(1)
H 19B	0.98440	-0.26740	1.24604	0.4(3)
H 19C	0.97480	-0.21130	1.37114	0.1(2)

$T=\exp[-2\pi^2 U]$, U=U(iso) or [U(11)+U(22)+U(33)]/3

Table 12. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **9**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Pt1	0.0184(5)	0.0324(5)	0.0255(5)	0.0009(4)	0.0067(3)	-0.0024(4)
Ge2	0.029(1)	0.050(1)	0.037(1)	0.003(1)	0.016(1)	-0.003(1)
Ge3	0.031(1)	0.043(1)	0.038(1)	-0.004(1)	0.009(1)	-0.014(1)
S 4	0.062(3)	0.046(3)	0.114(5)	-0.017(3)	0.046(4)	-0.006(3)
S 5	0.050(3)	0.076(4)	0.053(3)	0.007(3)	-0.001(2)	0.006(3)
N 6	0.06(1)	0.05(1)	0.05(1)	0.01(1)	0.03(1)	0.02(1)
C 7	0.07(1)	0.05(1)	0.07(1)	0.02(1)	0.06(1)	0.01(1)
C 8	0.019(8)	0.066(12)	0.033(9)	-0.014(8)	0.001(7)	-0.003(8)
C 9	0.05(1)	0.09(2)	0.17(3)	-0.02(2)	0.06(2)	-0.01(2)
C 10	0.03(1)	0.12(2)	0.16(3)	-0.01(1)	0.03(2)	-0.06(2)
C 11	0.03(1)	0.12(2)	0.07(2)	0.01(1)	-0.02(1)	0.00(2)
C 12	0.09(2)	0.12(3)	0.05(1)	-0.02(2)	0.03(1)	-0.04(2)
C 13	0.07(2)	0.03(1)	0.13(3)	0.00(1)	0.01(2)	-0.02(1)
C 14	0.06(1)	0.08(2)	0.08(2)	0.02(1)	0.02(1)	-0.03(1)
C 15	0.07(2)	0.11(2)	0.07(2)	0.02(2)	0.05(1)	0.03(2)
C 16	0.08(2)	0.07(2)	0.07(2)	0.02(1)	0.03(1)	0.04(1)
C 17	0.5(1)	0.3(1)	0.3(1)	0.4(1)	0.3(1)	0.3(1)
C 18	0.26(6)	0.13(4)	0.10(3)	-0.02(5)	-0.01(4)	0.06(3)
C 19	0.17(5)	0.11(3)	0.23(6)	-0.05(4)	0.02(5)	0.10(4)

Table 13. Intramolecular Distances (Å) with Esd's in Parentheses for **9**

atom	atom	distance	atom	atom	distance
Pt1	- Ge2	2.506(2)	Pt1	- Ge2	2.506(2)
Pt1	- C 7	1.98(3)	Ge2	- C 14	1.94(3)
Ge2	- C 8	2.020(18)	Ge2	- C 15	1.98(3)
Ge3	- C 8	2.014(16)	Ge3	- C 13	1.99(3)
Ge3	- C 12	1.97(3)	S 4	- C 8	1.85(2)
S 4	- C 9	1.80(3)	S 5	- C 8	1.783(19)
S 5	- C 11	1.79(3)	N 6	- C 7	1.14(3)
N 6	- C 16	1.42(4)	C 16	- C 17	1.45(9)
C 19	- C 16	1.45(7)	C 18	- C 16	1.43(6)
C 10	- C 9	1.54(5)	C 10	- C 11	1.53(5)

Table 14. Intramolecular Angles (deg) with Esd's in Parentheses for **9**

atom	atom	atom	angle	atom	atom	atom	angle
Ge2	- Pt1	- Ge2'	180.0	Ge2	- Pt1	- Ge3	72.7(1)
Ge2	- Pt1	- Ge3'	107.3(1)	Ge2	- Pt1	- C 7	90.7(7)
Ge2	- Pt1	- C 7'	89.3(7)	Ge3	- Pt1	- Ge3'	180.0
Ge3	- Pt1	- C 7	90.8(7)	Ge3	- Pt1	- C 7'	89.2(7)
C 7	- Pt1	- C 7'	180.0	Pt1	- Ge2	- C 14	117.2(8)
Pt1	- Ge2	- C 8	94.9(5)	Pt1	- Ge2	- C 15	115.4(8)
C 14	- Ge2	- C 8	115.4(10)	C 14	- Ge2	- C 15	106.6(12)
C 8	- Ge2	- C 15	106.8(10)	Pt1	- Ge3	- C 12	116.7(10)
Pt1	- Ge3	- C 8	95.6(6)	Pt1	- Ge3	- C 13	117.9(10)
C 8	- Ge3	- C 13	108.8(10)	C 8	- Ge3	- C 12	109.4(11)
C 13	- Ge3	- C 12	107.5(15)	C 8	- S 4	- C 9	101.4(12)
C 8	- S 5	- C 11	102.2(11)	C 7	- N 6	- C 16	177.9(22)
Pt1	- C 7	- N 6	176.5(20)	Ge2	- C 8	- Ge3	94.5(7)
Ge2	- C 8	- S 4	116.1(9)	Ge2	- C 8	- S 5	115.2(11)
Ge3	- C 8	- S 4	110.4(10)	Ge3	- C 8	- S 5	107.9(9)
S 4	- C 8	- S 5	111.1(9)	C 9	- C 10	- C 11	113.0(24)
S 4	- C 9	- C 10	113.6(23)	S 5	- C 11	- C 10	115.5(21)
N 6	- C 16	- C 19	108.9(32)	N 6	- C 16	- C 18	109.8(29)
N 6	- C 16	- C 17	107.0(34)	C 19	- C 16	- C 18	109.9(42)
C 19	- C 16	- C 17	114.7(42)	C 18	- C 16	- C 17	106.5(44)

References and Notes

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Chapter 4

Synthesis of Organosilicon Macrocycles. Palladium-Catalyzed Ring-Enlargement Oligomerization of Cyclic Disilanes via Si–Si σ-Bond Metathesis

Abstract: Bis(*t*-alkyl isocyanide)palladium(0) complexes catalyzed a ring-enlargement oligomerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane through Si–Si σ-bond metathesis to give cyclic oligomers up to the 40-membered octamer. The cyclic structure of the tetramer was established by a single-crystal X-ray diffraction method, which showed that the four Si–Si bonds of the tetramer were in a close to parallel arrangement. Reactivities of the dimer, trimer, and tetramer in the presence of bis(*t*-butyl isocyanide)palladium(0) revealed that the present Si–Si σ-bond metathesis proceeded reversibly, in which the –$Me_2Si(CH_2)_3SiMe_2$– unit of the disilacyclopentane was successively inserted into the Si–Si bond of the oligomer to give higher oligomers. Intermediary 6-membered bis(organosilyl)bis(*t*-alkyl isocyanide)-palladium complex, which arose from oxidative addition of the disilacyclopentane onto bis(*t*-alkyl isocyanide)palladium(0), was isolated and characterized by single-crystal X-ray method. The insertion of the –$Me_2Si(CH_2)_3SiMe_2$– unit also occurred with linear disilanes and digermane to give linear oligomers. The cyclic trimer and tetramer reacted with 2,6-diisopropylphenyl isocyanide in the presence of $Pd(OAc)_2$ to afford 18-membered triimine and 24-membered-ring tetraimine, respectively, in which the isocyanides were inserted into all the Si–Si linkages. Oxidation of the cyclic oligomers with trimethylamine oxide gave the corresponding cyclic oligo(disiloxane)s in quantitative yields. Unexpected polymerization of the disilacyclopentane occurred in the presence of the (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) catalyst to give poly($Me_2Si(CH_2)_3SiMe_2$) with high molecular weights.

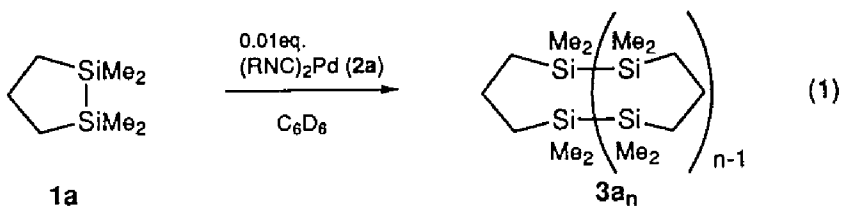
Introduction

Much attention has been focused on the design and synthesis of organic macrocycles containing heteroatoms and functional groups as functional molecules.[1] Introduction of electropositive elements such as Group 14 metals instead of electronegative elements into organic macrocycles with appropriate arrangement may lead to the development of new functional molecules. Especially, in view of the intriguing chemical and physical properties of Si–Si σ-bonds,[2] an efficient synthesis of macrocycles with regularly arranged Si–Si bonds may be desired. Palladium-catalyzed Si–Si σ-bond metathesis of cyclic disilanes seemed to provide a convenient method for preparation of macrocycles containing Si–Si bonds in the ring. However, palladium(0)–phosphine catalyst has been successfully applied only to cyclodimerization of cyclic 4- and 5-membered disilanes through the Si–Si σ-bond metathesis.[3–5]

In chapter 2, the author described a selective intramolecular Si–Si σ-bond metathesis of some bis(disilanyl)methanes catalyzed by bis(*t*-butyl isocyanide)palladium(0). The use of *t*-alkyl isocyanide ligands on palladium was crucially important for the activation of the Si–Si bonds.[6] Based on this activation, the author found that a catalytic amount of bis(*t*-butyl isocyanide)palladium(0) induced intermolecular Si–Si σ-bond metathesis of 1,1,2,2-tetramethyl-1,2-disilacyclopentane to lead to ring-enlargement oligomerization that gave macrocycles with regularly arranged Si–Si bonds.[7] In this chapter, it is described full details of the oligomerization of the disilacyclopentane, in which cyclic bis(organosilyl)bis(*t*-alkyl isocyanide)palladium(II) complex is involved as an intermediate. The author also presents the synthesis of linear oligo- and poly(disilanes) by palladium-catalyzed reactions of the 5-membered cyclic disilane. The cyclic oligomers thus prepared were further elaborated by insertion reactions and oxidation of the Si–Si linkages to give new functionalized organosilicon macrocycles.

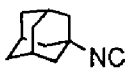
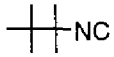
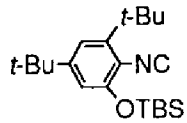
Results and Discussion

Ring-Enlargement Oligomerization of Cyclic Disilanes. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (**1a**) was reacted in the presence of 1 mol% of (*t*-BuNC)$_2$Pd(0) (**2a**) in C_6D_6 under argon in an NMR sample tube fitted with a rubber



1a $3a_n$ (1)

Table 1. Oligomerization of **1a** in the presence of $(RNC)_2Pd(0)$ (**2**) in benzene-d_6

entry	catalyst **2**	isocyanide	time (d), temp (°C)	ratio of oligomers $3a_n$ %							total yield %
				n = 2	3	4	5	6	7	8	
1	**2a**	*t*-BuNC	6, 50	9	44	30	12	5	0		66
2[a]	**2a**	*t*-BuNC	6, 80	26	41	22	7	4	0		53
3[b]	**2a**	*t*-BuNC	6, 80	32	44	18	6	0			41
4	**2b**		6, 80	10	24	26	15	10	8	6	62
5	**2c**		4, 80	81	19	0					27
6	**2d**	*i*-PrNC	6, 50	50	40	10	0				50
7	**2e**	2,6-XyNC	6, 50	91	9	0					46
8	**2f**		6, 50	100	0						46

[a] Addition of *t*-BuNC (1 equiv based on **2a**). [b] Addition of *t*-BuNC (2 equiv based on **2a**).

septum (eq 1; Table 1, entry 1). Though no reaction took place at room temperature, heating the mixture at 50°C resulted in slow conversion of **1a** into a mixture of oligomeric products, which included the literature-known cyclic dimer $3a_2$. After 6 days at this temperature, the oligomeric products were subjected to gel permeation chromatography to separate and isolate the cyclic oligomers $3a_n$ up to 30 membered hexamer. The cyclic structure of the tetramer $3a_4$ was established by single-crystal X-ray diffraction, which showed that the four Si–Si bonds in the ring were in a nearly

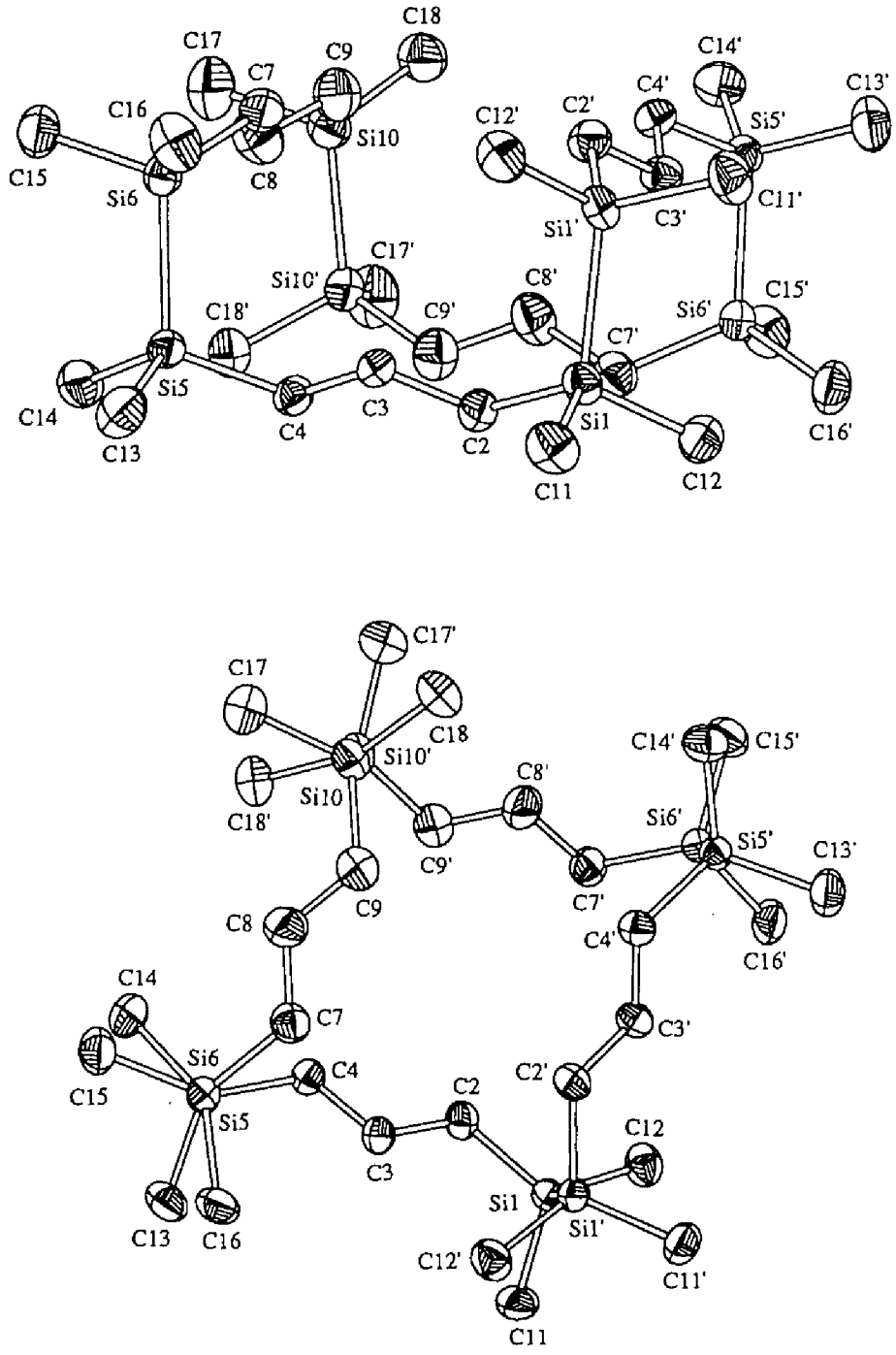
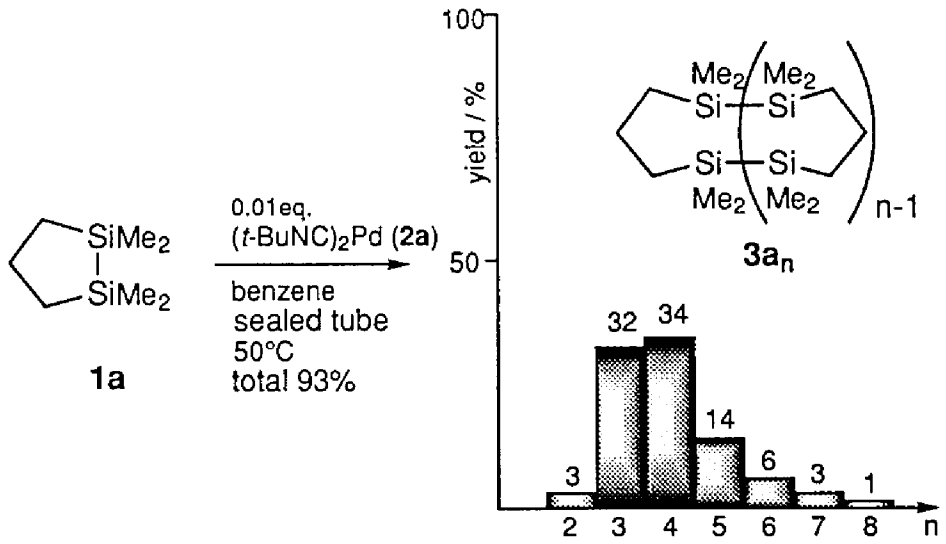


Figure 1. Crystal structure of the tetramer **3a**$_4$. (side view, top and top view, bottom) The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

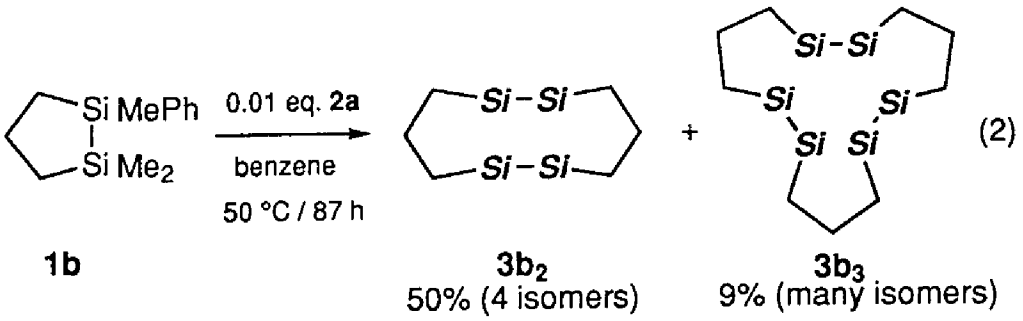
parallel arrangement (Figure 1). The oligomerization was significantly retarded by addition of a small amount (1 or 2 equiv based on palladium) of *t*-butyl isocyanide, although the reaction at 80°C gave the cyclic oligomers in nearly the same distribution (entries 2, 3). Among the various isocyanide examined, *t*-alkyl isocyanides except for 1,1,2,2-tetramethylpropyl isocyanide (in catalyst **2c**), which might be too bulky for the reaction to proceed, were the ligand of choice giving higher oligomers (entries 4, 5). Use of *sec*-alkyl isocyanide as well as aryl isocyanides resulted in formation of the oligomers only up to the tetramer $\mathbf{3a_4}$ (entries 6–8).

The yields of the oligomers were largely improved by carrying out the reaction in a sealed tube under higher concentration (see experimental section). Thus, in the presence of **2a**, a mixture of oligomers $\mathbf{3a_n}$ were obtained in 93% total yield, consisting of the dimer $\mathbf{3a_2}$ (3%), trimer $\mathbf{3a_3}$ (32%), tetramer $\mathbf{3a_4}$ (34%), pentamer $\mathbf{3a_5}$ (14%), hexamer $\mathbf{3a_6}$ (6%), heptamer $\mathbf{3a_7}$ (3%), and octamer $\mathbf{3a_8}$ (1%) (Scheme 1).

Scheme 1.



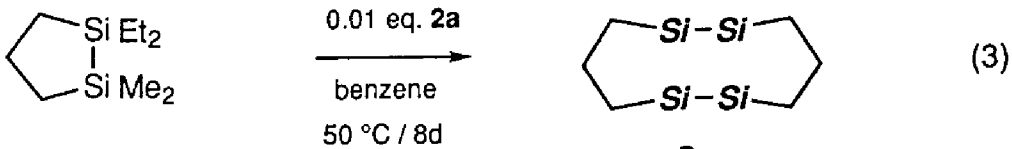
Unlike the reaction of **1a**, the cyclic disilanes **1b–g** showed much lower reactivities. 1,2-Disilacyclopentane **1b** gave dimer $\mathbf{3b_2}$ (50% yield, 3:3:2:2 mixture of 4 regio- and stereoisomers) and trimer $\mathbf{3b_3}$ (9% yield, many isomers), while **1c** gave only dimer $\mathbf{3c_2}$ under the condition identical with that employed for **1a** (eqs 2, 3). Other cyclic disilanes **1d–g** listed in Chart 1 failed to give oligomers.



1b

$3b_2$
50% (4 isomers)

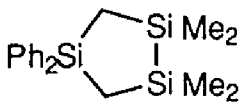
$3b_3$
9% (many isomers)



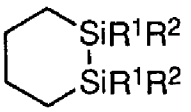
1c

$3c_2$
12% (2 isomers)

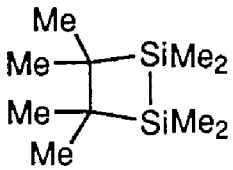
Chart 1



1d



1e ($R^1 = R^2 = Me$)
1f ($R^1 = Me$, $R^2 = OMe$)

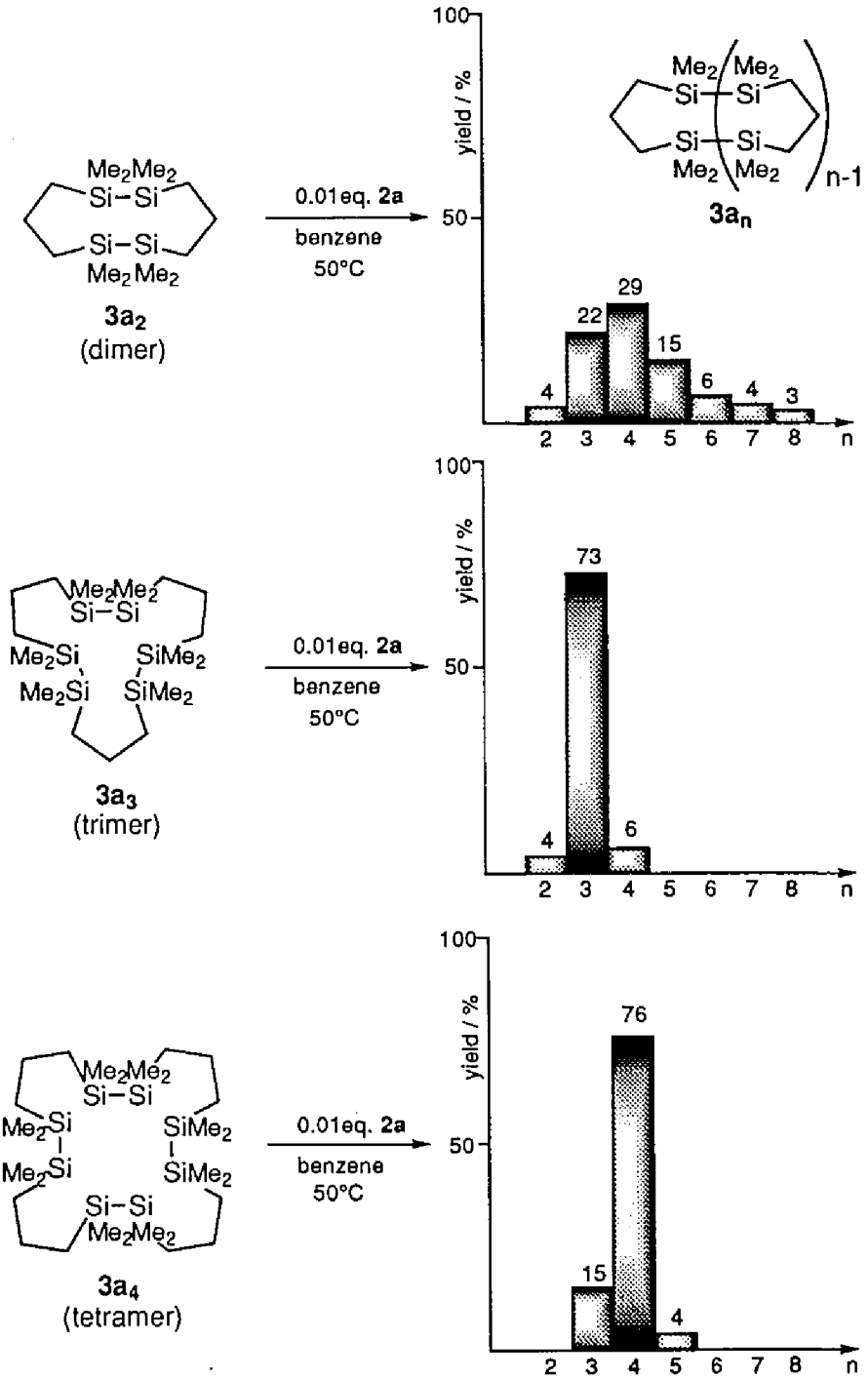


1g

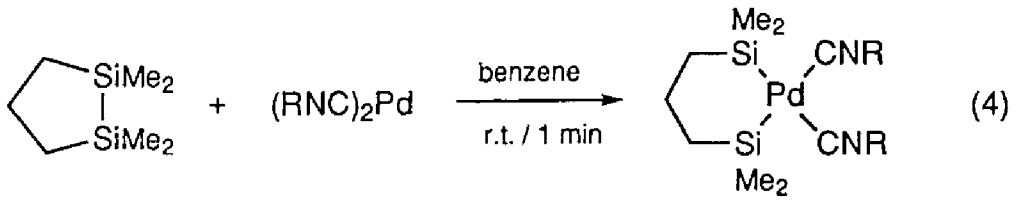
Mechanistic Interpretation. Treatment of the isolated oligomer $3a_2$, $3a_3$, or $3a_4$ under the reaction conditions employed for the oligomerization of **1a** revealed that the present ring-enlargement oligomerization was reversible (Scheme 2). Thus, the reaction starting with the dimer $3a_2$ afforded a mixture of oligomers in a distribution almost identical to that of the reaction with **1a**. Deoligomerization of the dimer followed by oligomerization of the resultant **1a** may be presumed. The cyclic trimer $3a_3$ and tetramer $3a_4$ underwent the deoligomerization and oligomerization only to the (n-1)mer and (n+1)mer, respectively, to a lesser extent. These findings imply that

the cyclooligomerization did not proceed by σ-bond metathesis between the two oligomers produced, but between the 5-membered cyclic disilane **1a** and the oligomers.

Scheme 2.



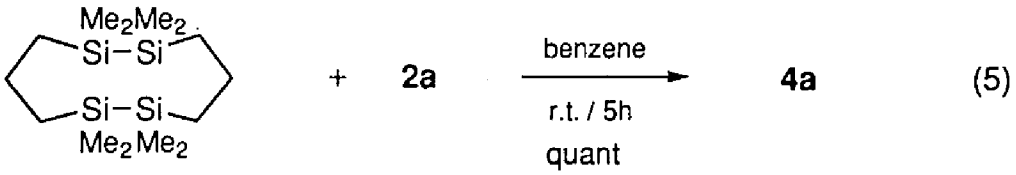
Concerning the intermediary palladium species, we found that **2a** reacted with **1a** at room temperature to give 6-membered cyclic bis(organosilyl)bis(*t*-butyl isocyanide)palladium(II) complex **4a** (eq 4). This very rapid, quantitative formation of **4a** may also be involved in the catalytic cycle of the oligomerization. A structure of the corresponding adamantyl isocyanide complex **4b** was determined by a single-crystal X-ray diffraction study (Figure 2). In the square planer complex, the angle Pd(1)–Si(2)–C(17) (>125°) was relatively large for sp_3 hybridization on the Si atoms.



(4)

1a **2a** (R = *t*-Bu) **4a** (R = *t*-Bu)
b (R = 1-adamantyl) **b** (R = 1-adamantyl)

The reaction of the dimer $\mathbf{3a_2}$ with 2 equiv of **2a** at room temperature was also noteworthy, it slowly gave the complex **4a** in quantitative yield (eq 5), while the tetramer $\mathbf{3a_4}$ failed to give **4a**. Presumably, the arrangement of the Si–Si bonds of the dimer was more appropriate than that of the tetramer for intramolecular metathesis of the Si–Si bonds in the ring (see chapter 2), which resulted in deoligomerization giving the (n-1)mer and **4a**.



$\mathbf{3a_2}$ (dimer)

(5)

A schematic illustration is presented for the ring-enlargement oligomerization of **1a** (Scheme 3). Oxidative addition of **1a** onto **2a** affords 6-membered bis(organosilyl)palladium complex **4**, which may react with the Si–Si bond of **1a** or the oligomers via five centered activation, to give higher cyclic oligomers. Though

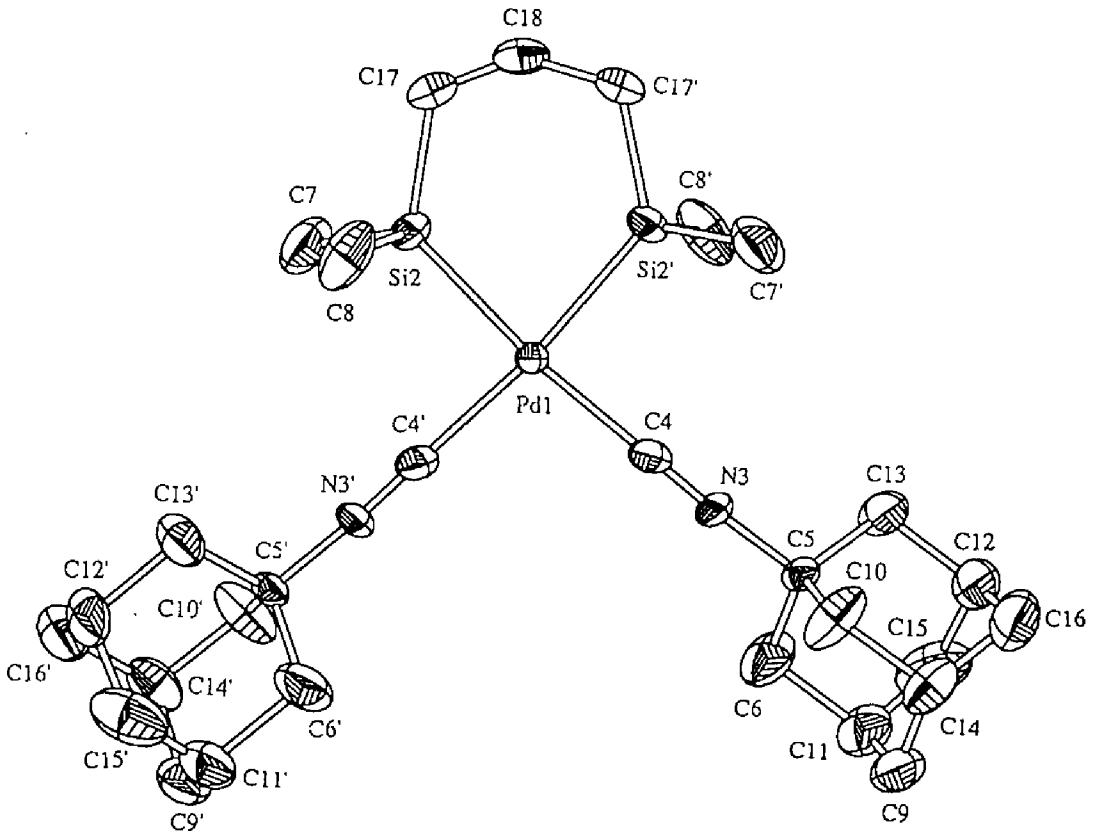
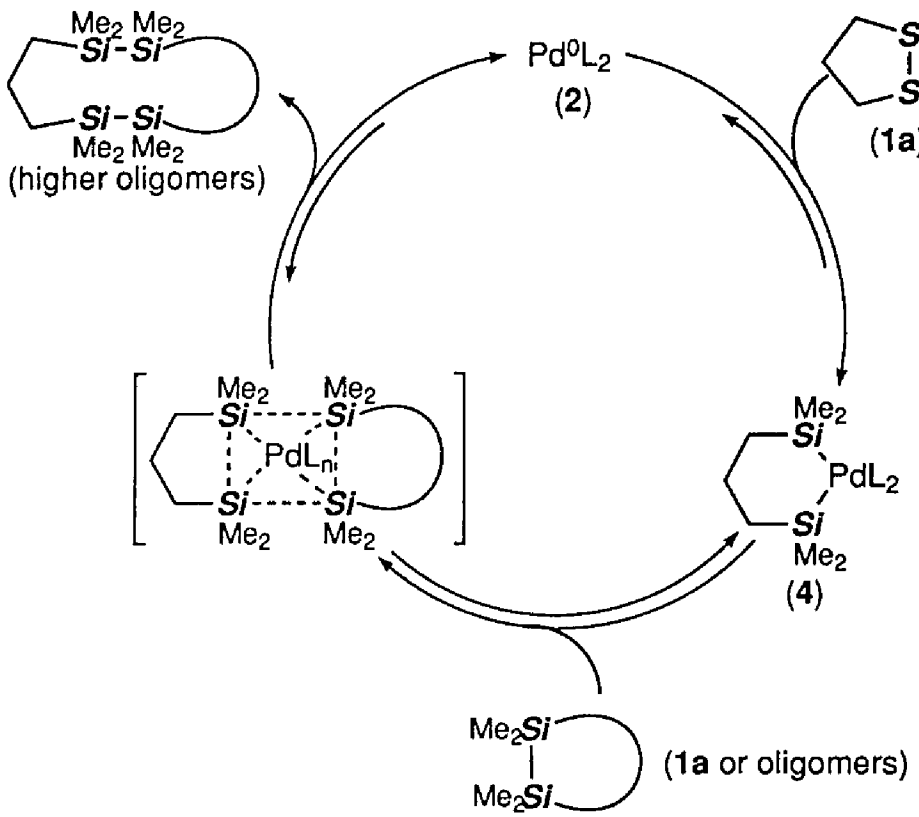


Figure 2. Crystal structure of **4b**. One of the two orientations of the disordered C(18) is shown. The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Pd(1)–Si(2) = 2.358(5), Pd(1)–C(4) = 2.059(16), Si(2)–Pd(1)–Si(2') = 85.8(2), Si(2)–Pd(1)–C(4') = 88.3(5), C(4)–Pd(1)–C(4') = 97.6(6), Pd(1)–Si(2)–C(17) = 126.3(9).

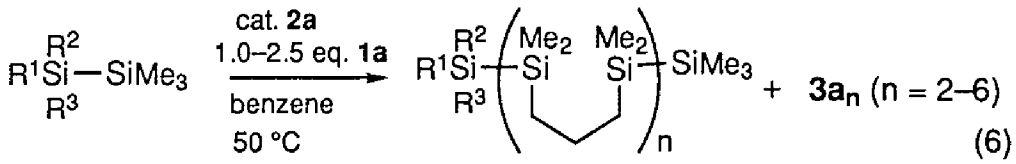
the cycle is reversible, the monomer **1a** is completely consumed to produce higher oligomers, since the oligomers higher than the cyclic trimer hardly undergo deoligomerization by intramolecular metathesis.

Scheme 3.



Oligomerization of 1a with Linear Disilanes. Cross oligomerization of **1a** with any linear disilanes according to the mechanism shown in Scheme 3 may expand synthetic utilities of the present metathesis. We found that linear disilanes **5** underwent insertion of **1a** to give acyclic cross-oligomerization products **6** along with the cyclic oligomers $\mathbf{3a}_n$ derived from the ring-enlargement oligomerization of **1a** (eq 6). In the reaction of hexamethyldisilane (**5a**) with 1 equiv of **1a**, tris(disilane) $\mathbf{6a}_2$ (n = 2) was detected by mass spectroscopy, though it could not be separated from the cyclic oligomers $\mathbf{3a}_n$ because of their low polarity. Use of the disilanes **5b–d** bearing phenyl or isopropoxy group made isolation of the oligomeric, linear products

$\mathbf{6_n}$ possible (Table 2). In the cases with **5b** and **5d**, insertion of **1a** into the Si–Si bonds of the linear disilanes occurred preferentially over the ring-enlargement oligomerization of **1a** (entries 1, 3).



5a ($R^1R^2R^3 = Me_3$)
b ($R^1R^2R^3 = PhMe_2$)
c ($R^1R^2R^3 = Ph_2Me$)
d ($R^1R^2R^3$ = (*i*-PrO)PhMe)

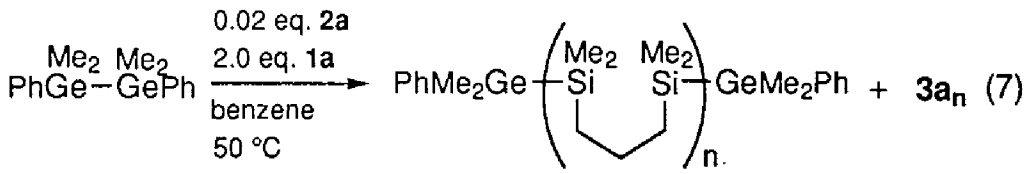
$\mathbf{6a_n}$ (detected by MASS)
$\mathbf{b_n}$ (n = 1–7)
$\mathbf{c_n}$ (n = 1–5)
$\mathbf{d_n}$ (n = 1–6)

Table 2. Cross Oligomerization of **1a** with Linear Disilanes

entry	5	time (d)	Linear Oligomers $\mathbf{6_n}$ / %yield[a]							Total Yield[a]	Selectivity[b] $\mathbf{6_n}$: $\mathbf{3a_n}$
			n = 1	2	3	4	5	6	7		
1[c]	**b**	2	30	20	9	4	1.4	0.5	0.2	65	67 : 33
2[c]	**c**	6	33	13	5	0.9	0.3			52	46 : 54
3[d]	**d**	3	22	20	12	6	3	1.4		64	66 : 34

[a] Isolated yields based on the linear disilanes **5**. [b] Ratios of the yields based on **1a**. [c] 2.0 equiv of 1a was used. [d] 2.5 equiv of 1a was used

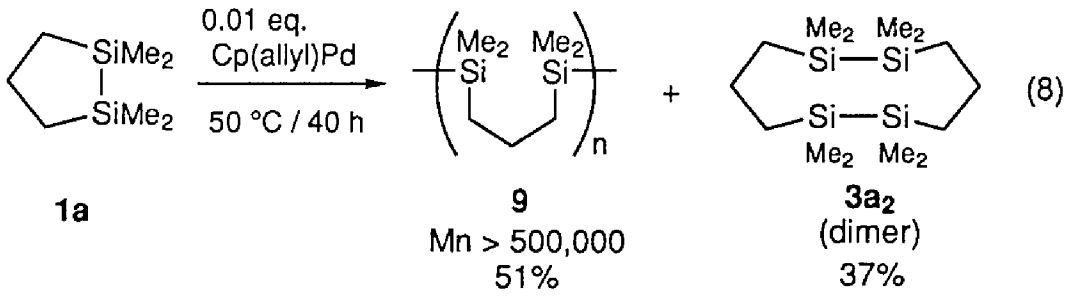
Noteworthy was that insertion of **1a** into 1,1,2,2-tetramethyl-1,2-diphenyldigermane (**7**) also took place to give a mixture of oligomers $\mathbf{8_n}$ (n = 1–6) bearing the dimethylphenylgermyl groups at the both ends (eq 7).



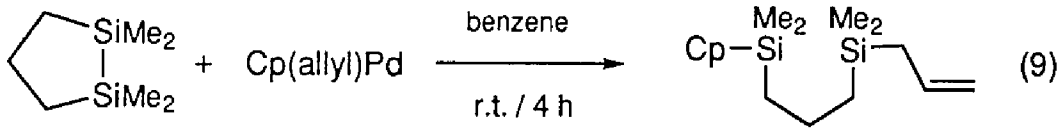
7

$\mathbf{8_n}$ (n = 1–6, 65%)

Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (1a). Of particular interest is that unlike bis(*t*-butyl isocyanide)palladium(0) (**2a**), (η^5-cyclopetadienyl)(η^3-allyl)palladium(II) catalyst induced polymerization of **1a** to give polymers **9** with very high molecular weights (51%, Mn > 500 000), which were accompanied only by the cyclic dimer $\mathbf{3a_2}$ (37%) (eq 8). No other oligomers were found. A separate experiment indicated that $\mathbf{3a_2}$ once isolated remained intact in the polymerization condition employing the Cp(allyl)Pd catalyst. A similar polymerization has also been reported by Suzuki's[8] and Tanaka's[9] group, who carried out the reaction of **1a** in the presence of palladium-phosphine complexes. The mechanistic discrepancy between the polymerization and the ring-enlargement oligomerization is not reasonably explained at this moment. It may be relevant to the mechanism that a stoichiometric reaction of (η^5-cyclopetadienyl)(η^3-allyl)palladium(II) with **1a** gave a ring-opening product **10** (eq 9).



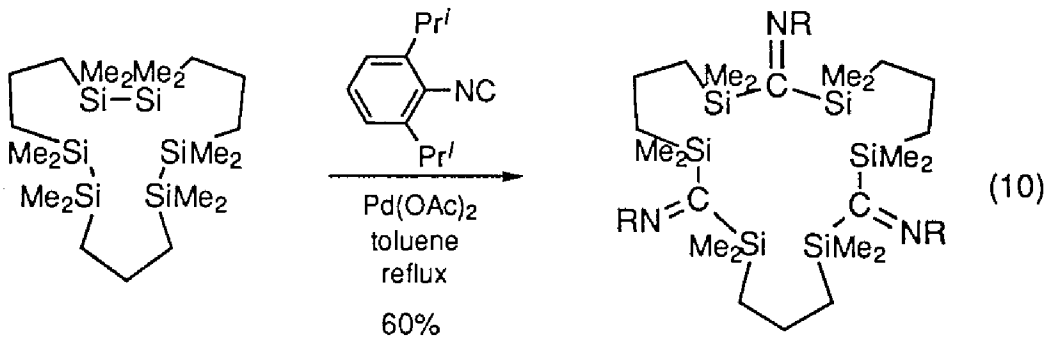
1a — **9**, Mn > 500,000, 51% — **3a₂** (dimer), 37%



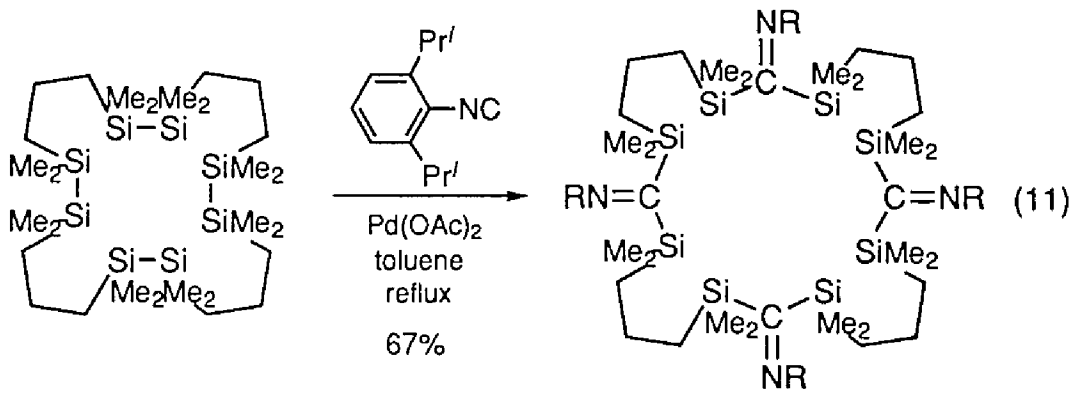
1a — **10** (57%)

Synthesis of Cyclic Organosilicon Compounds via Insertion Reactions with Si–Si Linkages of the Cyclic Oligomers. The cyclic oligomers thus far prepared, which contain Si–Si linkages in the ring, were further elaborated by virtue of the high but controllable reactivities of Si–Si toward transition metal complex catalysts, as demonstrated by insertion reactions of unsaturated molecules into the Si–Si bonds. Thus, in the presence of $Pd(OAc)_2$ catalyst, 2,6-diisopropylphenyl isocyanide inserted into all the Si–Si bonds of the trimer and tetramer to give 18-membered triimine **11a** and 24-membered tetraimine **11b**, respectively (eqs 10,

11).[10] Single-crystal X-ray diffraction studies of **11a** and **11b** showed planar triangle and lozenge shapes, respectively, with their each side occupied by the $-Me_2Si(CH_2)_3SiMe_2-$ unit (Figures 3, 4).



3a$_3$ **11a** (R = 2,6-Diisopropylphenyl)



3a$_4$ **11b** (R = 2,6-Diisopropylphenyl)

Unexpectedly, reaction of the trimer with phenylacetylene in the presence of a palladium catalyst prepared from $Pd(OAc)_2$ and 1,1,2,2-tetramethylbutyl isocyanide did not give the corresponding cyclic trienes, but resulted in formation of cyclic monoene **12a** and dienes **12b**, in which the one or two Si–Si linkages remained unchanged (eq 12).[11] The isolated cyclic **12b** failed to undergo further insertion of phenylacetylene.

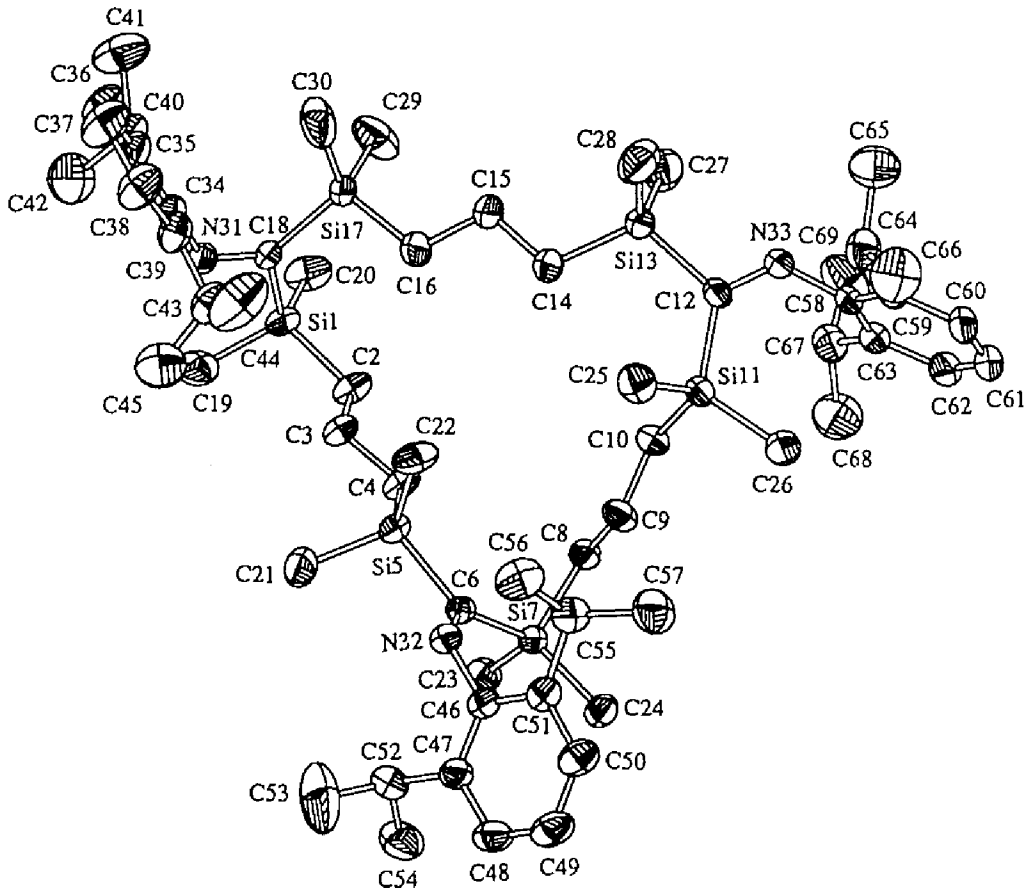


Figure 3. Crystal structure of **11a**. The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

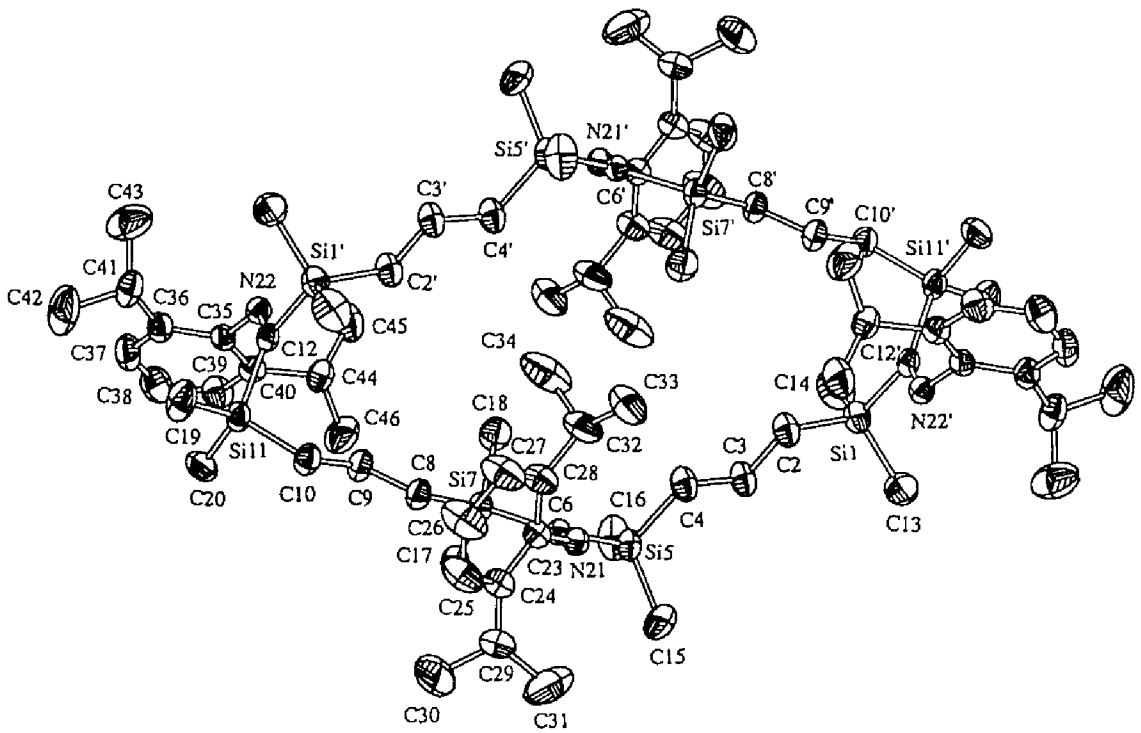
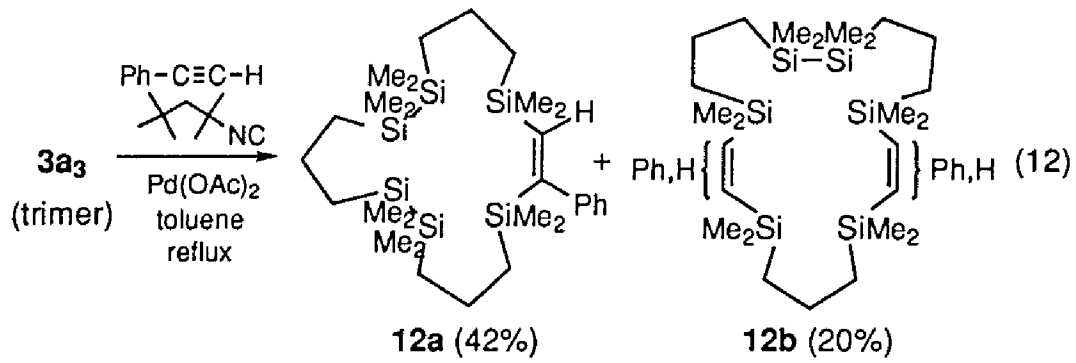
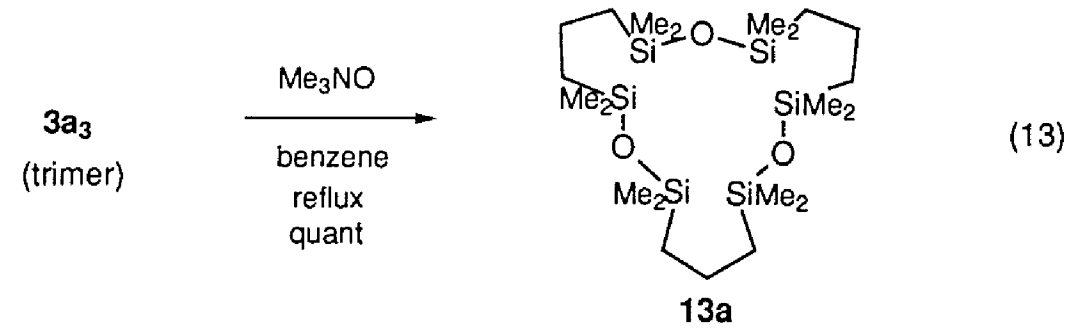
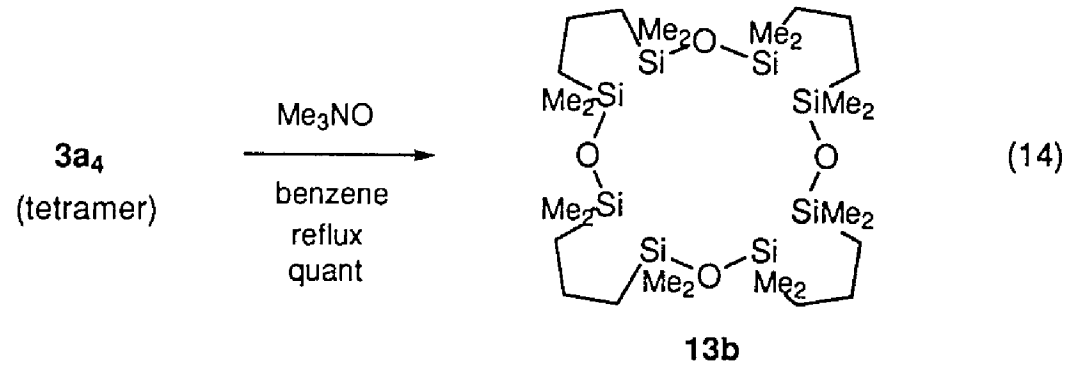


Figure 4. Crystal structure **11b**. The thermal elipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



The cyclic oligomers also underwent insertion of oxygen atoms by oxidation of the Si–Si linkages with trimethylamine oxide in refluxing benzene.[12] The reactions of the trimer and tetramer cleanly proceeded without ring-opening, affording tri(disiloxane) **13a** and tetra(disiloxane) **13b**, respectively, in quantitative yield (eqs 13, 14).





Conclusion

Oligomeric- as well as polymeric organosilicon compounds with regularly arranged Si–Si linkages were synthesized from 1,1,2,2-tetramethyl-1,2-disilacyclopentane in the presence of palladium catalyst. Especially, ring-enlargement oligomerization of the cyclic disilane gave cyclic oligomers up to 40-membered octamer. Bis(*t*-alkyl isocyanide)palladium(0) complexes, which gives a cyclic bis(organosilyl)palladium intermediate on reaction with 1,2-disilacyclopentanes, were essential for the ring-enlargement oligomerization and the cross-oligomerization with linear disilanes.

Experimental Section

General. All reactions were carried out under a dry nitrogen or an argon atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^{1}H, ^{13}C, and ^{29}Si spectra were recorded on a Varian VXR-200. Proton chemical shifts (ppm) are referenced to internal residual solvent protons: $CDCl_3$, 7.25; C_6D_6, 7.20. Carbon chemical shifts (ppm) are referenced to the carbon signal of the deuterated solvents: $CDCl_3$, 77.0; C_6D_6, 128.0. Silicon chemical shifts are referenced to the signals of tetramethylsilane. IR spectra were recorded with a Hitachi 270-30 spectrometer. Electron impact mass spectra (MS) were recorded with a JEOL LMS-D300 spectrometer. Fast atom bombardment mass spectra (FABMS) were recorded with a JEOL JMS-SX102A spectrometer. Preparative gel permeation chromatography was performed with JAI LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1H and -2H columns.

Preparation of Bis(isonitrile)palladium(0) (2). The procedure reported by Otsuka et.al.[13] was followed with slight modification. To a pentane solution of (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (117 mg, 0.55 mmol) was added the corresponding isonitrile (2.2 mmol) at -10°C under argon. After 10 min., removal of supernatant liquid gave bis(isonitrile)palladium(0) **2** as orange solid, which was washed twice with pentane, dried in vacuo, and used for further reaction. Complex **2** was obtained nearly quantitatively, though the yield was not determined for the each reaction.

Oligomerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (1a) in the

presence of 2. a) General Procedure for the Reactions in an NMR Sample Tube. A mixture of bis(*t*-alkyl isocyanide)palladium(0) **2** (5 μmol) and 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**1a**) (79 mg, 0.5 mmol) in benzene-d_6 (0.6 mL) was heated at 50°C–80°C under argon for the period described in Table 1. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers $\mathbf{3a_n}$, which was subjected to preparative gel permeation chromatography to separate each oligomer. **b) Procedure for the Reaction in a Sealed Tube.** A mixture of **1a** (158 mg, 1.0 mmol) and **2** (freshly prepared 0.5 M solution in benzene, 20 μL, 10 μmol) was heated at 50°C under argon in a sealed tube for 90h. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers $\mathbf{3a_n}$, which was subjected to preparative gel permeation chromatography to separate dimer $\mathbf{3a_2}$ (4 mg, 3 %), trimer $\mathbf{3a_3}$ (51 mg, 32 %), tetramer $\mathbf{3a_4}$ (53 mg, 34 %), pentamer $\mathbf{3a_5}$ (22 mg, 14 %), hexamer $\mathbf{3a_6}$ (10 mg, 6 %), heptamer $\mathbf{3a_7}$ (4 mg, 3 %), and octamer $\mathbf{3a_8}$ (2 mg, 1 %).

1,1,2,2,6,6,7,7-Octamethyl-1,2,6,7-tetrasilacyclodecane ($\mathbf{3a_2}$): mp 71.0–72.0 °C; ^{1}H NMR (C_6D_6) δ 0.14 (s, 24 H), 0.80–0.88 (m, 8 H), 1.52–1.70 (m, 4 H); ^{13}C NMR (C_6D_6) δ -2.7, 20.3, 21.5; IR (KBr) 2916, 1248, 796 cm^{-1}; MS (20 eV) *m/z* 316 (M^+). Anal. Calcd for $C_{14}H_{36}Si_4$: C, 53.08; H, 11.45. Found: C, 52.80; H, 11.51.

1,1,2,2,6,6,7,7,11,11,12,12-Dodecamethyl-1,2,6,7,11,12-hexasilacyclopentadecane ($\mathbf{3a_3}$): mp 34.5–35.0°C; ^{1}H NMR (C_6D_6) δ 0.17 (s, 36 H), 0.81–0.91 (m, 12 H), 1.50–1.66 (m, 6 H); ^{13}C NMR (C_6D_6) δ -3.2, 21.1, 21.6; IR (neat) 2956, 1246, 800 cm^{-1}; MS (20 eV) *m/z* 474 (M^+). Anal. Calcd for $C_{21}H_{54}Si_6$: C, 53.08; H, 11.45. Found: C, 52.81; H, 11.62.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17-Hexadecamethyl-1,2,6,7,11,12,16,17-octasilacycloeicosane ($\mathbf{3a_4}$): mp 94.5–95.5 °C; ^{1}H NMR (C_6D_6) δ 0.19 (s, 48 H), 0.81–0.91 (m, 16 H), 1.51–1.67 (m, 8 H); ^{13}C NMR (C_6D_6) δ -3.6, 20.6, 20.9; IR (KBr) 2912, 1246, 828 cm^{-1}; MS (20 eV) *m/z* 632 (M^+). Anal. calcd for $C_{28}H_{72}Si_8$: C, 53.08; H, 11.45. Found: C, 53.03; H, 11.53.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22-Eicosamethyl-1,2,6,7,11,12,16,17,21,22-decasilacyclopentacosane ($\mathbf{3a_5}$): ^{1}H NMR (C_6D_6) δ 0.21 (s, 60 H), 0.83–0.92 (m, 20 H), 1.53–1.69 (m, 10 H); ^{13}C NMR (C_6D_6) δ -3.5, 20.5,

20.7; IR (neat) 2956, 1246, 792 cm^{-1}; MS (20 eV) *m/z* 790 (M^+). Anal. Calcd. for $C_{35}H_{90}Si_{10}$: C, 53.08; H, 11.45. Found: C, 52.80; H, 11.60.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27-Tetracosamethyl-1,2,6,7,11,12,16,17,21,22,26,27-dodecasilacyclotriacontane ($3a_6$): mp 46.0–47.0 °C; ^1H NMR (C_6D_6) δ 0.22 (s, 72 H), 0.84–0.94 (m, 24 H), 1.54–1.71 (m, 12 H); ^{13}C NMR (C_6D_6) δ -3.5, 20.5, 20.7; IR (neat) 2956, 1246, 790 cm^{-1}; FABMS *m/z* 948 (M^+). Anal. Calcd. for $C_{42}H_{108}Si_{12}$: C, 53.08; H, 11.45. Found: C, 53.09; H, 11.58.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27,31,31,32,32-Octacosamethyl-1,2,6,7,11,12,16,17,21,22,26,27,31,32-tetradecasilacyclopentatriacontane ($3a_7$): ^1H NMR (C_6D_6) δ 0.22 (s, 84 H), 0.84–0.93 (m, 28 H), 1.53–1.72 (m, 14 H); ^{13}C NMR (C_6D_6) δ -3.5, 20.5, 20.7; IR (neat) 2956, 1246, 792 cm^{-1}; FABMS *m/z* 1107 (M^+).

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27,31,31,32,32,36,36,37,37-Dotriacontamethyl-1,2,6,7,11,12,16,17,21,22,26,27,31,32,36,37-hexadecasilacyclotetracontane ($3a_8$): ^1H NMR (C_6D_6) δ 0.23 (s, 96 H), 0.85–0.93 (m, 32 H), 1.54–1.72 (m, 16 H); ^{13}C NMR (C_6D_6) δ -3.4, 20.5, 20.7; IR (neat) 2956, 1245, 792 cm^{-1}; FABMS *m/z* 1266 (M^+).

Oligomerization of 1,2,2-Trimethyl-1-phenyl-1,2-disilacyclopentane (1b) in the Presence of 2a. A mixture of **1b** (220 mg, 1.0 mmol) and **2a** (freshly prepared 0.25 M solution in benzene, 40 μL, 10 μmol) was stirred at 50°C under argon in a sealed tube for 87h. The cooled mixture was passed through a short column of silica gel (hexane/ether = 10/1) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers $\mathbf{3b_n}$, which was subjected to preparative gel permeation chromatography to separate dimers $\mathbf{3b_2}$ (a mixture of 4 isomers, 110 mg, 50 %), trimers $\mathbf{3b_3}$ (a mixture of many isomers, 19 mg, 9 %), and **1b** (78 mg, 35 % recovered). Recrystallization of the dimers from ethanol gave the one of four isomers, which was determined to be (1*R**,6*S**)-1,2,2,6,7,7-hexamethyl-1,6-diphenyl-1,2,6,7-tetrasilacyclodecane by single-crystal X-ray method (see Figure 4).

$\mathbf{3b_2}$: ^1H NMR for the (1*R**,6*S**) isomer ($CDCl_3$) δ -0.02 (s, 6 H), 0.10 (s, 6 H), 0.35 (s, 6 H), 0.74–1.26 (m, 8 H), 1.64–1.80 (m, 4 H), 7.30–7.36 (m, 6 H), 7.40–7.48 (m, 4 H); MS (23 eV) *m/z* 440 (M^+). Elemental analysis was carried out for the mixture of the isomers. Anal Calcd for $C_{24}H_{40}Si_4$: C, 65.38; H, 9.14. Found: C,

65.44; H, 9.37.

$3b_3$: MS (23 eV) *m/z* 660 (M^+); Anal Calcd for $C_{36}H_{60}Si_6$: C, 65.38; H, 9.14. Found: C, 65.44; H, 9.32.

Oligomerization of 1,1-Diethyl-2,2-dimethyl-1,2-disilacyclopentane (1c) in the Presence of 2a. A mixture of **1c** (186 mg, 1.0 mmol) and **2a** (freshly prepared 0.25 M solution in benzene, 40 μL, 10 μmol) was stirred at 50°C under argon in a sealed tube for 8 days. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. After evaporation of the resulting colorless solution, the residue was subjected to preparative gel permeation chromatography to furnish dimer **$3c_2$** (a mixture of two isomers, 23 mg, 12 %). **$3c_2$**: ^{1}H NMR (C_6D_6) δ 0.15 (s, 12 H for the minor isomer), 0.20 (s, 12 H for the major isomer), 0.60–0.78 (m, 8 H for both isomers), 0.82–0.94 (m, 8 H for both isomers), 1.05 (t, J = 7.4 Hz, 12 H for the major isomer), 1.06 (t, J = 7.7 Hz, 12 H for the minor isomer), 1.56–1.74 (m, 4 H for both isomers); MS (23 eV) *m/z* 372 (M^+). Anal Calcd for $C_{18}H_{44}Si_4$: C, 57.98; H, 11.89. Found: C, 57.80; H, 12.10.

General Procedure for the Reactions of Isolated Oligomers $3a_2$, $3a_3$, and $3a_4$. The oligomer **$3a_n$** (79 mg, 0.50 mmol of $-Me_2Si(CH_2)_3SiMe_2-$ unit), **2a** (freshly prepared 0.1 M solution in benzene, 50 μL, 5 μmol), and benzene (0.2 mL) was stirred at 50°C under argon for 40h. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers, which was subjected to preparative gel permeation chromatography to separate into each oligomer.

Preparation of Bis(organosilyl)palladium–isocyanide complex 4b. To a benzene (1 mL) solution of **2b** (0.2 mmol) was added **1a** (32 mg, 0.2 mmol) at room temperature under an argon atmosphere. After 30 min., evaporation of the solvent followed by recrystallization from benzene/pentane (1/4) afforded **4b** (114 mg, 97%) as a crystalline solid. **4b**: mp 218°C (dec.); ^{1}H NMR (C_6D_6) δ 0.79 (s, 12 H), 1.16–1.25 (m, 4 H), 1.26 (br, 12 H), 1.66 (br, 6 H), 1.80 (br, 12 H), 2.28–2.42 (m, 2 H); ^{13}C NMR (C_6D_6) δ 7.1, 22.3, 22.8, 28.8, 35.3, 43.0, 56.1, 146.7; ^{29}Si NMR (C_6D_6) δ -0.3; IR (benzene) 2146 cm^{-1}. Anal Calcd for $C_{29}H_{48}N_2PdSi_2$: C, 59.31; H, 8.24; N, 4.77. Found: C, 59.15; H, 8.37; N, 4.74.

Stoichiometric Reaction of Cyclic Dimer $3a_2$ with 2a. To a benzene-d_6 (0.3 mL) solution of **2a** (0.05 mmol) in an NMR sample tube was added a benzene-d_6 (0.3 mL) solution of **$3a_2$** (7.9 mg, 0.025 mmol) at room temperature under an argon atmo-

sphere. After 5 h at room temperature, ^{1}H NMR showed quantitative formation of **4a**.

Reaction of Hexamethyldisilane (5a) with 1a in the Presence of 2a. A mixture of **5a** (37 mg, 0.25 mmol), **1a** (40 mg, 0.25 mmol), and **2a** (freshly prepared 0.1 M solution in benzene, 50 μL, 5 μmol) in benzene (0.4 mL) was heated at 50 °C for 20h. The cooled mixture was passed through a short column of silica gel (hexane). After evaporation of the solvent, the residue was subjected to preparative GPC to give five fractions. The third fraction was analyzed by mass spectroscopy, which revealed the existence of $\mathbf{6a_2}$ (*m/z* 462) along with cyclic tetramer $\mathbf{3a_4}$ (*m/z* 632) .

Reaction of Pentamethylphenyldisilane (5b) with 1a in the Presence of 2a. A mixture of **5b** (83 mg, 0.4 mmol), **1a** (158 mg, 1.0 mmol), and **2a** (freshly prepared 0.1 M solution in benzene, 100 μL, 10 μmol) in benzene (0.4 mL) was heated in sealed tube at 50 °C for 90h. Preparative TLC (hexane) afforded mixtures of $\mathbf{6b_n}$ and cyclic oligomers $\mathbf{3a_n}$ (n = 2–6, 29 mg, 0.18 mmol of $-Me_2Si(CH_2)_3SiMe_2-$ unit). The mixture of $\mathbf{6b_n}$ was subjected to preparative gel permeation chromatography to give $\mathbf{6b_1}$ (30 mg, 20 %), $\mathbf{6b_2}$ (28 mg, 13 %), $\mathbf{6b_3}$ (22 mg, 8 %), $\mathbf{6b_4}$ (16 mg, 5 %), $\mathbf{6b_5}$ (8 mg, 2 %), $\mathbf{6b_6}$ (4 mg, 1 %), and $\mathbf{6b_7}$ (3 mg, 0.6 %). Elemental analyses were carried out for $\mathbf{6b_1}$, $\mathbf{6b_2}$ and $\mathbf{6b_3}$.

$\mathbf{6b_1}$; ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 6 H), 0.03 (s, 15 H), 0.34 (s, 6 H), 0.56–0.70 (m, 4 H), 1.24–1.40 (m, 2 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.3, -4.0, -3.6, -2.0, 19.8, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m/z* 366 (M^+). Anal Calcd for $C_{18}H_{38}Si_4$: C, 58.94; H, 10.44. Found: C, 59.00; H, 10.35.

$\mathbf{6b_2}$; ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 6 H), 0.01 (s, 6 H), 0.02 (s, 6 H), 0.04 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56–0.70 (m, 8 H), 1.22–1.44 (m, 4 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -4.0, -3.8, -3.6, -2.0, 19.78, 19.81, 19.9, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m/z* 524 (M^+). Anal Calcd for $C_{25}H_{56}Si_6$: C, 57.17; H, 10.75. Found: C, 57.35; H, 10.97.

$\mathbf{6b_3}$; ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 6 H), 0.00 (s, 6 H), 0.017 (s, 6 H), 0.022 (s, 12 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56–0.70 (m, 12 H), 1.24–1.46 (m, 6 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -4.0, -3.8, -3.6, -2.0, 19.79, 19.85, 19.91, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m/z* 682 (M^+). Anal Calcd for $C_{32}H_{74}Si_8$: C, 56.22; H, 10.91. Found: C, 56.12; H, 11.11.

$\mathbf{6b_4}$; ^{1}H NMR ($CDCl_3$) δ -0.01 (s, 6 H), 0.01 (s, 6 H), 0.02 (s, 30 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56–0.70 (m, 16 H), 1.22–1.48 (m, 8 H), 7.30–7.36

(m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -4.0, -3.8, -3.6, -2.0, 19.76, 19.85, 19.90, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_5$; ^1H NMR ($CDCl_3$) δ -0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 42 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.33 (s, 6 H), 0.56–0.70 (m, 20 H), 1.22–1.46 (m, 10 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -4.0, -3.8, -3.6, -2.0, 19.75, 19.85, 19.89, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_6$; ^1H NMR ($CDCl_3$) δ -0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 60 H), 0.04 (s, 9 H), 0.33 (s, 6 H), 0.56–0.70 (m, 24 H), 1.24–1.46 (m, 12 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -4.0, -3.8, -3.6, -2.0, 19.8, 19.9, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_7$; ^1H NMR ($CDCl_3$) δ -0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 72 H), 0.04 (s, 9 H), 0.33 (s, 6 H), 0.56–0.70 (m, 28 H), 1.24–1.48 (m, 14 H), 7.30–7.36 (m, 3 H), 7.42–7.48 (m, 2 H).

Reaction of 1,2,2,2-Tetramethyl-1,1-diphenyldisilane (5c) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **5c** (135 mg, 0.50 mmol) with **1a** (158 mg, 1.0 mmol) in the presence of **2a** (10 μmol) was carried out to give **6c$_1$** (71 mg, 33 %), **6c$_2$** (39 mg, 13 %), **6c$_3$** (18 mg, 5.0 %), **6c$_4$** (4.2 mg, 0.9 %), and **6c$_5$** (1.4 mg, 0.3 %).

6c$_1$: ^1H NMR (C_6D_6) δ 0.05 (s, 6 H), 0.11 (s, 9 H), 0.22 (s, 6 H), 0.65 (s, 3 H), 0.58–0.71 (m, 2 H), 0.78–0.94 (m, 2 H), 1.36–1.52 (m, 2 H), 7.15–7.30 (m, 6 H), 7.55–7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.3, -3.5, -2.0, 19.7, 19.8, 20.1, 127.8, 128.6, 134.8, 137.6; MS (23 eV) *m/z* 428 (M+). Anal Calcd for $C_{23}H_{40}Si_4$: C, 64.41; H, 9.40. Found: C, 64.04; H, 9.39.

6c$_2$: ^1H NMR (C_6D_6) δ 0.12 (s, 6 H), 0.14 (s, 6 H), 0.15 (s, 6 H), 0.16 (s, 9 H), 0.24 (s, 6 H), 0.66 (s, 3 H), 0.68–0.92 (m, 8 H), 1.42–1.64 (m, 4 H), 7.15–7.32 (m, 6 H), 7.55–7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.2, -3.91, -3.86, -3.5, -2.0, 19.7, 19.9, 20.1, 127.8, 128.7, 134.8, 137.6. Anal Calcd for $C_{30}H_{58}Si_6$: C, 61.35; H, 9.95. Found: C, 61.31; H, 10.11.

6c$_3$: ^1H NMR (C_6D_6) δ 0.12 (s, 6 H), 0.15 (s, 6 H), 0.16 (s, 15 H), 0.20 (s, 12 H), 0.24 (s, 6 H), 0.66 (s, 3 H), 0.76–0.92 (m, 12 H), 1.46–1.68 (m, 6 H), 7.15–7.30 (m, 6 H), 7.55–7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.5, -4.2, -3.9, -3.8, -3.5, -2.0, 19.7, 19.8, 19.9, 20.1, 20.2, 127.8, 128.6, 134.8, 137.6. Anal Calcd for $C_{37}H_{76}Si_8$: C, 59.60; H, 10.27. Found: C, 59.72; H, 10.49.

6c$_4$: ^1H NMR (C_6D_6) δ 0.13 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 15 H), 0.210 (s, 6

H), 0.213 (s, 18 H), 0.25 (s, 6 H), 0.67 (s, 3 H), 0.78–0.94 (m, 16 H), 1.48–1.71 (m, 8 H), 7.15–7.30 (m, 6 H), 7.55–7.65 (m, 4 H).

6c$_5$: ^{1}H NMR (C_6D_6) δ 0.13 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 12 H), 0.21 (s, 9 H), 0.22 (br s, 30 H), 0.25 (s, 6 H), 0.67 (s, 3 H), 0.79–0.93 (m, 20 H), 1.47–1.68 (m, 10 H), 7.15–7.31 (m, 6 H), 7.53–7.65 (m, 4 H).

Reaction of 1-Isopropoxy-1,2,2,2-tetramethyl-1-phenyldisilane (5d) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **5d** (126 mg, 0.50 mmol) with **1a** (228 mg, 1.3 mmol) in the presence of **2a** (13 μmol) was carried out to give **6d$_1$** (18 mg, 22 %), **6d$_2$** (33 mg, 20 %), **6d$_3$** (30 mg, 12 %), **6d$_4$** (20 mg, 6 %), **6d$_5$** (11 mg, 3 %), and **6d$_6$** (6.6 mg, 1.4 %).

6d$_1$: ^{1}H NMR (C_6D_6) δ 0.11 (s, 6 H), 0.14 (s, 9 H), 0.21 (s, 6 H), 0.57 (s, 3 H), 0.67–0.88 (m, 4 H), 1.15 (d, J = 6.1 Hz, 6 H), 1.42–1.62 (m, 2 H), 3.96 (septet, J = 6.1 Hz, 1 H), 7.18–7.33 (m, 3 H), 7.65–7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.3, -3.8, -2.0, -1.2, 19.7, 19.8, 19.9, 25.9, 26.0, 66.2, 127.7, 128.9, 133.6, 139.5. Anal Calcd for $C_{20}H_{42}OSi_4$: C, 58.46; H, 10.30. Found: C, 58.59; H, 10.57.

6d$_2$: ^{1}H NMR (C_6D_6) δ 0.14 (s, 6 H), 0.16 (s, 9 H), 0.17 (s, 6 H), 0.18 (s, 6 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.72–0.92 (m, 8 H), 1.15 (d, J = 6.1 Hz, 6 H), 1.46–1.66 (m, 4 H), 3.98 (septet, J = 6.1 Hz, 1 H), 7.20–7.35 (m, 3 H), 7.66–7.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -3.9, -3.84, -3.75, -2.0, -1.2, 19.7, 19.9, 20.1, 20.2, 25.9, 66.2, 127.7, 128.9, 133.6, 139.5. Anal Calcd for $C_{27}H_{60}OSi_6$: C, 56.92; H, 10.62. Found: C, 56.66; H, 10.43.

6d$_3$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.16 (s, 9 H), 0.17 (s, 6 H), 0.19 (s, 6 H), 0.198 (s, 6 H), 0.200 (s, 6 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.73–0.92 (m, 12 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.46–1.69 (m, 6 H), 3.94 (septet, J = 6.1 Hz, 1 H), 7.15–7.35 (m, 3 H), 7.65–7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -3.82, -3.75, -2.0, -1.2, 19.6, 19.8, 19.9, 20.1, 20.2, 25.90, 25.94, 66.2, 127.7, 128.9, 133.6, 139.5. Anal Calcd for $C_{34}H_{78}OSi_8$: C, 56.12; H, 10.80. Found: C, 56.25; H, 10.93.

6d$_4$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.17 (s, 9 H), 0.18 (s, 6 H), 0.19 (s, 6 H), 0.20 (s, 6 H), 0.21 (br s, 18 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.76–0.92 (m, 16 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.46–1.70 (m, 8 H), 3.90 (septet, J = 6.1 Hz, 1 H), 7.15–7.34 (m, 3 H), 7.65–7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -3.9, -3.8, -2.0, -1.3, 19.6, 19.8, 19.9, 20.1, 20.2, 25.89, 25.94, 66.2, 127.7, 128.9, 133.6, 139.5. Anal Calcd for $C_{41}H_{96}OSi_{10}$: C, 55.58; H, 10.92. Found: C, 55.61; H, 11.19.

6d$_5$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.17 (s, 9 H), 0.18 (s, 6 H), 0.20 (s, 6 H),

0.21 (s, 6 H), 0.22 (s, 30 H), 0.58 (s, 3 H), 0.72–0.93 (m, 20 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.45–1.71 (m, 10 H), 3.97 (septet, J = 6.1 Hz, 1 H), 7.15–7.36 (m, 3 H), 7.65–7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -4.2, -3.8, -2.0, -1.2, 19.6, 19.8, 20.2, 25.9, 66.2, 127.7, 128.9, 133.6, 139.5.

6d$_6$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 6 H), 0.17 (s, 9 H), 0.18 (s, 6 H), 0.19 (s, 6 H), 0.20 (s, 6 H), 0.21 (br s, 42 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.74–0.94 (m, 24 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.47–1.72 (m, 12 H), 3.96 (septet, J = 6.1 Hz, 1 H), 7.15–7.32 (m, 3 H), 7.66–7.73 (m, 2 H).

Reaction of 1,1,2,2-Tetramethyl-1,2-diphenyldigermane (7) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **7** (180 mg, 0.50 mmol) with **1a** (158 mg, 1.0 mmol) in the presence of **2a** (10 μmol) was carried out to give **8$_1$** (67 mg, 26 %), **8$_2$** (63 mg, 19 %), **8$_3$** (50 mg, 11 %), **8$_4$** (35 mg, 7.2 %), **8$_5$** (10 mg, 1.7 %), and **8$_6$** (5.1 mg, 0.8 %).

8$_1$: ^{1}H NMR (C_6D_6) δ 0.12 (s, 12 H), 0.48 (s, 12 H), 0.64–0.75 (m, 4 H), 1.27–1.46 (m, 2 H), 7.18–7.35 (m, 6 H), 7.43–7.59 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.1, -3.4, 19.6, 20.2, 127.6, 127.9, 133.5, 142.5; MS (23 eV) *m/z* 518 (M^+). Anal Calcd for $C_{23}H_{40}Ge_2Si_2$: C, 53.34; H, 7.78. Found: C, 53.22; H, 7.93.

8$_2$: ^{1}H NMR (C_6D_6) δ 0.13 (s, 12 H), 0.18 (s, 12 H), 0.51 (s, 12 H), 0.66–0.81 (m, 8 H), 1.35–1.59 (m, 4 H), 7.19–7.36 (m, 6 H), 7.47–7.58 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.1, -3.9, -3.3, 19.7, 20.0, 20.4, 127.6, 127.9, 133.5, 142.5; MS (23 eV) *m/z* 676 (M^+). Anal Calcd for $C_{30}H_{58}Ge_2Si_4$: C, 53.28; H, 8.64. Found: C, 53.00; H, 8.91.

8$_3$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 12 H), 0.18 (s, 24 H), 0.52 (s, 12 H), 0.70–0.88 (m, 12 H), 1.41–1.67 (m, 6 H), 7.21–7.34 (m, 6 H), 7.50–7.59 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -4.1, -3.9, -3.3, 19.7, 19.8, 20.0, 20.1, 20.4, 127.6, 127.9, 133.5, 142.6; MS (23 eV) *m/z* 834 (M^+). Anal Calcd for $C_{37}H_{76}Ge_2Si_6$: C, 53.24; H, 9.18. Found: C, 53.11; H, 9.43.

8$_4$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 12 H), 0.18 (s, 24 H), 0.21 (s, 12 H), 0.52 (s, 12 H), 0.70–0.91 (m, 16 H), 1.41–1.69 (m, 8 H), 7.15–7.32 (m, 6 H), 7.46–7.54 (m, 4 H).

8$_5$: ^{1}H NMR (C_6D_6) δ 0.17 (s, 12 H), 0.19 (s, 24 H), 0.22 (s, 24 H), 0.52 (s, 12 H), 0.72–0.93 (m, 20 H), 1.44–1.75 (m, 10 H), 7.19–7.35 (m, 6 H), 7.48–7.56 (m, 4 H).

8$_6$: ^{1}H NMR (C_6D_6) δ 0.17 (s, 12 H), 0.19 (s, 24 H), 0.22 (br s, 36 H), 0.53 (s, 12 H), 0.78–0.93 (m, 24 H), 1.46–1.72 (m, 12 H), 7.16–7.33 (m, 6 H), 7.47–7.58 (m,

4 H).

Polymerization of 1a in the Presence of Cp(π-allyl)Pd. A mixture of **1a** (158 mg, 1.0 mmol) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (2 mg, 10 μmol) was stirred at 50°C under argon for 40 h. The cooled gummy mixture was dissolved into $CHCl_3$ and passed through a filter to remove the palladium catalyst. Evaporation of the resulting colorless solution and separation by preparative gel permeation chromatography gave the cyclic dimer **3** (n = 2, 51 mg, 37 %) and polymers **9** (80 mg, 51 %). GPC analysis of the polymer showed its molecular weights > 500,000 (polystyrene standard). Spectral data for the polymers: ^{1}H NMR (C_6D_6) δ 0.25 (s, 12n H), 0.85–0.96 (m, 4n H), 1.56–1.74 (m, 2n H); ^{13}C NMR (C_6D_6) δ -3.6, 20.5, 20.7; IR (neat) 2960, 1246, 788 cm^{-1}.

Stoichiometric Reaction of 1a with Cp(π-allyl)Pd. A mixture of **1a** (32 mg, 0.2 mmol) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (42 mg, 0.2 mmol) was stirred at room temperature under argon for 4h. The mixture was passed through a short column of silica gel (hexane). Evaporation of the resulting colorless solution gave crude material, which was further purified by preparative HPLC to give pure **10** (30 mg, 57%). **10**: ^{1}H NMR (C_6D_6) for major positional isomer, i.e., 1-(2,4-cyclopentadienyl)-1,1,2,2-tetramethyl-2-(2-propenyl)disilane; δ -0.09 (s, 6 H), 0.01 (s, 6 H), 0.50–0.64 (m, 4 H), 1.28–1.45 (m, 2 H), 1.50 (dt, J = 8.2, 1.2 Hz, 2 H), 3.34 (br, 1 H), 4.89–5.02 (m, 2 H), 5.70–5.94 (m, 1 H), 6.46–6.74 (br, 4 H); ^{13}C NMR (C_6D_6) for the major positional isomer δ -3.9, -3.6, 18.9, 19.6, 20.2, 23.5, 51.4, 113.1, 130.6, 133.3, 135.3. HRMS calcd for $C_{15}H_{28}Si_2$: 264.1729. Found: 264.1744.

Synthesis of Cyclic Triimine 11a. A mixture of the trimer **3a$_3$** (79 mg, 0.17 mmol), 2,6-diisopropylphenylisocyanide (140 mg, 0.75 mmol), and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) in toluene (0.5 mL) was heated under reflux for 26 h. The cooled mixture was passed through a short column of Et_3N-pretreated Florisil (hexane) to remove the palladium catalyst. Crystallization from dry EtOH afforded triimine **11a** (103 mg, 60 %) as yellow crystals. **11a**; mp 156.0–157.0 °C (sealed tube); ^{1}H NMR (toluene-d_8, 100°C) δ 0.44 (s, 36 H), 1.28–1.56 (m, 12H), 1.50 (d, J = 6.6 Hz, 36 H), 1.74–2.00 (m, 6 H), 3.08–3.30 (m, 6 H), 7.24–7.46 (m, 9 H); IR (KBr) 3068, 2968, 1544, 1252, 830 cm^{-1}; FABMS *m/z* 1036 (M^+). Anal. Calcd. for $C_{60}H_{105}N_3Si_6$: C, 69.49; H, 10.21; N, 4.05. Found: C, 69.39; H, 10.48; N, 3.86.

Synthesis of Cyclic Tetraimine 11b. A mixture of the tetramer **3a$_4$** (63 mg, 0.1 mmol), 2,6-diisopropylphenylisocyanide (112 mg, 0.6 mmol), and $Pd(OAc)_2$

(4.5 mg, 0.02 mmol) in toluene (0.5 mL) was heated under reflux for 36 h. The cooled mixture was passed through a short column of Et_3N-pretreated Florisil (hexane) to remove the palladium catalyst. Crystallization from dry EtOH afforded tetraimine **11b** (92 mg, 67 %) as yellow crystals. **11b**; mp 150.0–151.0 °C (sealed tube); ^1H NMR (toluene-d_8, 90°C) δ 0.49 (s, 48 H), 1.20–1.45 (m, 16H), 1.51 (br s, 48 H), 1.76–1.98 (m, 8 H), 3.10–3.30 (m, 8 H), 7.25–7.46 (m, 12 H); IR (KBr) 3072, 2972, 1540, 1258, 1250, 1138, 928 cm^{-1}; FABMS *m/z* 1381 (M^+). Anal. Calcd. for $C_{80}H_{140}N_4Si_8$: C, 69.49; H, 10.21; N, 4.05. Found: C, 69.48; H, 10.44; N, 3.91.

Palladium-Catalyzed Reaction of the Cyclic Trimer with Phenylacetylene. To a mixture of $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (21 mg, 0.15 mmol) was added trimer **3a$_3$** (79 mg, 0.17 mmol) and phenylacetylene (77 mg, 0.75 mmol) under a nitrogen atmosphere. The mixture was stirred under reflux for 26 h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12b** (23 mg, 20%) and another fraction containing **12a**. The crude fraction was further purified by preparative GPC to give pure **12a** (40 mg, 42%).

12a: ^1H NMR ($CDCl_3$) δ 0.01 (s, 12 H), 0.04 (s, 6 H), 0.05 (s, 6 H), 0.10 (s, 6 H), 0.18 (s, 6 H), 0.60–0.86 (m, 12 H), 1.24–1.52 (m, 6 H), 6.42 (s, 1 H), 6.98–7.04 (m, 2 H), 7.14–7.30 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ -3.9, -3.8, -3.7, -0.5, 19.2, 19.3, 20.5, 20.6, 20.7, 21.1, 21.2, 22.1, 125.5, 126.3, 127.7, 148.7, 151.1, 164.1; IR (neat) 3064, 2960, 1490, 1248, 832 cm^{-1}. Anal. Calcd. for $C_{29}H_{60}Si_6$: C, 60.34; H, 10.48. Found: C, 60.10; H, 10.55.

12b (mixture of three isomers): ^1H NMR ($CDCl_3$) δ 0.01–0.21 (many singlets, 36 H), 0.64–0.90 (m, 12 H), 1.26–1.56 (m, 6 H), 6.41–6.44 (three singlets, 2H), 6.96–7.04 (m, 4 H), 7.14–7.30 (m, 6 H); IR (neat) 3080, 2960, 1490, 1250, 832 cm^{-1}. Anal. Calcd. for $C_{37}H_{66}Si_6$: C, 65.41; H, 9.79. Found: C, 65.21; H, 10.06.

Synthesis of Compound 13a. A mixture of the trimer **3a$_3$** (79 mg, 0.17 mmol) and trimethylamine oxide (38 mg, 0.5 mmol) in benzene (3 mL) was heated under reflux for 46 h. The reaction mixture was cooled to room temperature and then subjected to column chromatography on silica gel (hexane) to furnish tri(disiloxane) **13a** (87 mg, quantitative). **13a**; ^1H NMR (C_6D_6) δ 0.20 (s, 36 H), 0.82–0.92 (m, 12H), 1.58–1.78 (m, 6 H); ^{13}C NMR (C_6D_6) δ 0.76, 17.7, 23.2; IR (KBr) 2964, 1412, 1254, 1070 cm^{-1}; MS (23eV) *m/z* 522 (M^+). Anal. Calcd. for $C_{21}H_{54}O_3Si_6$: C, 48.21; H, 10.40. Found: C, 48.14; H, 10.60.

Synthesis of Compound 13b. By a procedure similar to that used for the synthesis of **13a**, reaction of the tetramer **3a$_4$** (79 mg, 0.125 mmol) with trimethylamine oxide (45 mg, 0.60 mmol) was carried out to give tetra(disiloxane) **13b** (87 mg, quantitative). **13b**; ^{1}H NMR (C_6D_6) δ 0.21 (s, 48 H), 0.85–0.95 (m, 16H), 1.56–1.75 (m, 8 H); ^{13}C NMR (C_6D_6) δ 0.77, 17.8, 23.3; IR (KBr) 2968, 1414, 1256, 1064 cm^{-1}; MS (23eV) *m/z* 696 (M^+). Anal. Calcd. for $C_{28}H_{72}O_4Si_8$: C, 48.21; H, 10.40. Found: C, 48.50; H, 10.66.

Single Crystal X-ray Analysis of 3a$_4$. Suitable single crystal of **3a$_4$** was grown from $CHCl_3$. A crystal of **3a$_4$** was mounted on a glass fiber using epoxy resin. Data collection was carried out on a Mac Science MXC3 diffractmeter with Mo Kα radiation (λ = 0.70930 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 2.27 cm^{-1}). The structure was solved by direct method and refined full-matrix least-squares procedure against $|F^2|$ with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 3. Final positional parameters are listed in Table 5. Anisotropic thermal parameters are given in Table 6. Intramolecular and intermolecular bond distances are presented in Table 7 and 8, respectively. Intramolecular and intermolecular bond angles are presented in Table 9 and 10, respectively.

Single Crystal X-ray Analysis of 4b. Suitable single crystal of **4b** was grown from benzene–pentane (4/1). A crystal of **4b** coated with silicon grease was mounted in a thin-walled glass capillary under an argon atmosphere. Data collection was carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization. The structure was solved by direct method and refined full-matrix least-squares procedure against $|F|$ with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for that on C(18) were included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters. The disordered C(18) was refined with occupation factor of 0.5. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 3. Final positional parameters are listed in

Table 11. Anisotropic thermal parameters are given in Table 12. Intramolecular bond distances are presented in Table 13. Intramolecular bond angles are presented in Table 14.

Single Crystal X-ray Analysis of 11a. Suitable single crystal of **11a** was grown from benzene–ethanol(1/5). A crystal of **11a** was mounted on a glass fiber using epoxy resin. Data collection was carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 12.94 cm^{-1}). The structure was solved by direct method and refined full-matrix least-squares procedure against $|F^2|$ with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for those on C(21) and C(53) were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 4. Final positional parameters are listed in Table 15. Anisotropic thermal parameters are given in Table 16. Intramolecular bond distances are presented in Table 17. Intramolecular bond angles are presented in Table 18.

Single Crystal X-ray Analysis of 11b. Suitable single crystal of **11b** was grown from benzene–ethanol (1/5). A crystal of **11b** was mounted on a glass fiber using epoxy resin. Data collection was carried out on a Mac Science MXC3 diffractmeter with Cu Kα radiation (λ = 1.54178 Å). The intensity data were corrected for Lorentzian polarization and absorption corrections by analytical function (μ = 12.81 cm^{-1}). The structure was solved by direct method and refined full-matrix least-squares procedure against $|F^2|$ with program package CrystanG (Mac Science). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except for those on C(30) and C(31) were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 4. Final positional parameters are listed in Table 19. Anisotropic thermal parameters are given in Table 20. Intramolecular and intermolecular bond distances are presented in Table 21 and 22, respectively. Intramolecular and intermolecular bond angles are presented in Table 23 and 24, respectively.

Table 3. Summary of Crystallographic Data for **3a$_4$** and **4b**

compound	**3a$_4$**	**4b**
formula	$C_{28}H_{72}Si_8$	$C_{29}H_{48}N_2PdSi_2$
formula weight	633.6	587.3
crystal system	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a, Å	21.700 (8)	22.761 (7)
b, Å	13.598 (6)	11.268 (3)
c, Å	15.336 (9)	14.379 (6)
α, deg		
β, deg	107.88 (4)	121.26 (2)
γ, deg		
cell vol, Å^3	4307 (3)	3152 (2)
Z	4	4
ρ(calcd), g cm^{-3}	0.98	1.24
F(000)	1408	1240
crystal size, mm	0.50 × 0.50 × 0.30	0.60 × 0.30 × 0.35
μ, cm^{-1}	2.27	57.239
diffractometer	Mac Science MXC3	Mac Science MXC3
monochromator	graphite	graphite
radiation	Mo Kα (λ = 0.71073 Å)	Cu Kα (λ = 1.54178 Å)
temp, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
2θmax, deg	50	130
reflns measured	5432	2999
independent reflns	4953	2641
reflns used	3417 ($F>3\sigma(F)$)	2380
no. of variables	277	182
R, *Rw*	0.065, 0.071	0.081, 0.108
goodness of fit	1.99	2.57
max δ/σ in final cycle	1.91	0.43
residual electron density (min, max) (e/Å^3)	-0.65, 0.86	-3.25, 2.58

Table 4. Summary of Crystallographic Data for **11a** and **11b**

compound	**11a**	**11b**
formula	$C_{60}H_{105}N_3Si_6$	$C_{80}H_{140}N_4Si_8$
formula weight	1037.0	1380.0
crystal system	orthorhombic	monoclinic
space group	*Pna*21 (No. 33)	*P*21/*a* (No. 14)
a, Å	18.862 (4)	18.603 (4)
b, Å	26.369 (4)	13.669 (3)
c, Å	13.889 (3)	18.345 (3)
α, deg		
β, deg		94.28 (2)
γ, deg		
cell vol, Å^3	6908 (2)	4652 (2)
Z	4	2
ρ(calcd), g cm^{-3}	1.00	0.99
F(000)	2280	1520
crystal size, mm	0.50 × 0.45 × 0.40	0.25 × 0.35 × 0.40
μ, cm^{-1}	12.94	12.81
diffractometer	Mac Science MXC3	Mac Science MXC3
monochromator	graphite	graphite
radiation	Cu Kα (λ = 1.54178 Å)	Cu Kα (λ = 1.54178 Å)
temp, K	293	293
scan type	$\omega/2\theta$	$\omega/2\theta$
2θmax, deg	130	130
reflns measured	6477	8584
independent reflns	5902	7768
reflns used	5730	7046
no. of variables	940	629
R, *Rw*	0.040, 0.039	0.068, 0.047
goodness of fit	1.22	1.90
max δ/σ in final cycle	0.98	0.90
residual electron density (min, max) (e/Å^3)	-0.15, 0.19	-0.26, 0.38

Table 5. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$) with Esd's in Parentheses for **3a**$_4$

atom	x	y	z	B(eq)
Si1	0.01430 (4)	-0.14832 (7)	-0.33044 (6)	4.20 (3)
Si5	-0.22017 (4)	-0.42978 (6)	-0.36580 (6)	3.95 (3)
Si6	-0.20339 (4)	-0.43968 (6)	-0.20678 (6)	4.08 (3)
Si10	0.00230 (5)	-0.71126 (8)	-0.17194 (7)	5.75 (4)
C 2	0.0525 (2)	-0.2688 (3)	-0.3784 (2)	4.7 (1)
C 3	-0.1120 (2)	-0.2987 (2)	-0.3511 (2)	4.20 (9)
C 4	-0.1450 (2)	-0.3938 (2)	-0.3951 (2)	4.34 (9)
C 7	-0.1179 (2)	-0.4711 (3)	-0.1410 (3)	5.3 (1)
C 8	-0.0938 (2)	-0.5698 (3)	-0.1758 (4)	6.8 (1)
C 9	0.0241 (2)	-0.5953 (3)	-0.1301 (3)	6.9 (1)
C 11	0.0586 (2)	-0.1267 (4)	-0.3698 (3)	6.2 (1)
C 12	-0.0739 (2)	-0.0472 (3)	-0.3777 (3)	6.0 (1)
C 13	-0.2504 (3)	-0.5510 (3)	-0.4208 (3)	6.7 (1)
C 14	-0.2839 (2)	-0.3348 (3)	-0.4151 (3)	6.1 (1)
C 15	-0.2256 (2)	-0.3193 (3)	-0.1641 (3)	6.7 (1)
C 16	-0.2585 (2)	-0.5380 (4)	-0.1870 (3)	6.8 (1)
C 17	0.0886 (3)	-0.7355 (5)	-0.0964 (4)	8.9 (2)
C 18	-0.0499 (2)	-0.8150 (4)	-0.1554 (4)	7.2 (2)
H 7A	-0.108 (2)	-0.486 (3)	-0.081 (3)	5.21 (0)
H 4A	-0.155 (2)	-0.392 (3)	-0.454 (3)	4.14 (0)
H 4B	-0.114 (2)	-0.450 (3)	-0.381 (2)	4.14 (0)
H 3A	-0.101 (2)	-0.306 (3)	-0.292 (3)	4.03 (0)
H 7B	-0.090 (2)	-0.415 (3)	-0.145 (3)	5.21 (0)
H 2A	-0.066 (2)	-0.264 (3)	-0.447 (3)	4.48 (0)
H 18A	-0.048 (2)	-0.872 (4)	-0.189 (3)	6.82 (0)
H 2B	-0.027 (2)	-0.326 (3)	-0.366 (3)	4.48 (0)
H 15A	-0.202 (2)	-0.265 (3)	-0.176 (3)	6.43 (0)
H 14A	-0.293 (2)	-0.336 (3)	-0.479 (3)	5.94 (0)
H 14B	-0.271 (2)	-0.276 (3)	-0.386 (3)	5.94 (0)
H 14C	-0.319 (2)	-0.356 (3)	-0.400 (3)	5.94 (0)
H 18B	-0.045 (2)	-0.832 (3)	-0.086 (3)	6.82 (0)
H 9A	0.001 (2)	-0.526 (3)	-0.152 (3)	6.69 (0)
H 15B	-0.214 (2)	-0.327 (3)	-0.103 (3)	6.43 (0)
H 3B	-0.147 (2)	-0.244 (3)	-0.365 (2)	4.03 (0)
H 15C	-0.274 (2)	-0.303 (3)	-0.195 (3)	6.43 (0)
H 16A	-0.255 (2)	-0.540 (4)	-0.133 (3)	6.48 (0)
H 16B	-0.251 (2)	-0.596 (3)	-0.209 (3)	6.48 (0)
H 11A	0.083 (2)	-0.174 (3)	-0.353 (3)	5.91 (0)
H 12A	-0.114 (2)	-0.060 (3)	-0.367 (3)	5.84 (0)
H 11B	0.045 (2)	-0.108 (3)	-0.441 (3)	5.91 (0)
H 13A	-0.246 (2)	-0.553 (4)	-0.470 (3)	6.40 (0)
H 18C	-0.093 (2)	-0.797 (4)	-0.197 (3)	6.82 (0)
H 11C	0.084 (2)	-0.074 (3)	-0.339 (3)	5.91 (0)
H 12B	-0.074 (2)	-0.032 (3)	-0.433 (3)	5.84 (0)
H 16C	-0.310 (2)	-0.536 (3)	-0.227 (3)	6.48 (0)
H 13B	-0.216 (2)	-0.607 (3)	-0.388 (3)	6.40 (0)
H 13C	-0.290 (2)	-0.571 (3)	-0.411 (3)	6.40 (0)
H 8A	-0.118 (2)	-0.621 (3)	-0.160 (3)	6.77 (0)
H 12C	-0.060 (2)	0.017 (3)	-0.347 (3)	5.84 (0)
H 17A	0.107 (3)	-0.670 (4)	-0.096 (4)	8.77 (0)
H 17B	0.111 (3)	-0.781 (4)	-0.120 (4)	8.77 (0)
H 9B	-0.024 (2)	-0.591 (3)	-0.052 (3)	6.69 (0)
H 8B	-0.098 (2)	-0.571 (3)	-0.244 (3)	6.77 (0)
H 17C	0.079 (3)	-0.728 (4)	-0.045 (4)	8.77 (0)

Table 6. Anisotropic Thermal Parameters (Å²) with Esd's in Parentheses for **3a₄**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Si1	0.0410 (4)	0.0636 (6)	0.0505 (9)	-0.0049 (4)	0.0144 (4)	0.0030 (4)
Si5	0.0516 (4)	0.0478 (6)	0.0453 (9)	-0.0061 (4)	0.0144 (4)	-0.0004 (4)
Si6	0.0529 (4)	0.0497 (6)	0.0486 (9)	-0.0001 (4)	0.0194 (4)	0.0003 (4)
Si10	0.0685 (6)	0.0702 (7)	0.076 (1)	-0.0082 (5)	0.0347 (5)	-0.0059 (6)
C 2	0.053 (2)	0.063 (2)	0.057 (2)	-0.006 (2)	0.021 (2)	-0.002 (2)
C 3	0.052 (2)	0.058 (2)	0.046 (2)	-0.006 (1)	0.019 (1)	0.001 (2)
C 4	0.056 (2)	0.054 (2)	0.051 (2)	-0.004 (2)	0.022 (2)	-0.003 (2)
C 7	0.062 (2)	0.068 (2)	0.064 (2)	0.004 (2)	0.015 (2)	0.012 (2)
C 8	0.077 (3)	0.074 (3)	0.094 (3)	0.010 (2)	0.007 (2)	0.006 (3)
C 9	0.072 (2)	0.085 (3)	0.097 (3)	0.002 (2)	0.026 (2)	-0.002 (2)
C 11	0.062 (2)	0.097 (3)	0.074 (3)	-0.012 (2)	0.033 (2)	-0.000 (2)
C 12	0.065 (2)	0.069 (2)	0.082 (3)	0.000 (2)	0.015 (2)	0.016 (2)
C 13	0.113 (3)	0.068 (2)	0.064 (3)	-0.028 (2)	0.031 (2)	-0.014 (2)
C 14	0.062 (2)	0.079 (3)	0.079 (3)	0.010 (2)	0.014 (2)	0.013 (2)
C 15	0.099 (3)	0.075 (3)	0.073 (3)	0.014 (2)	0.031 (2)	-0.010 (2)
C 16	0.094 (3)	0.092 (3)	0.070 (3)	-0.028 (2)	0.040 (2)	0.001 (2)
C 17	0.081 (3)	0.140 (6)	0.101 (4)	-0.012 (3)	0.013 (3)	0.007 (4)
C 18	0.090 (3)	0.080 (3)	0.103 (4)	-0.010 (2)	0.049 (3)	0.001 (3)

Table 7. Intramolecular Distances (Å) with Esd's in Parentheses for **3a₄**

atom	atom	distance	atom	atom	distance
Si1	- C 12	1.874 (4)	Si6	- C 15	1.880 (5)
Si1	- C 2	1.882 (4)	Si10	- C 9	1.858 (5)
Si1	- C 11	1.882 (5)	Si10	- C 18	1.874 (5)
Si5	- C 14	1.873 (4)	Si10	- C 17	1.903 (5)
Si5	- C 13	1.876 (4)	C 2	- C 3	1.531 (5)
Si5	- C 4	1.886 (4)	C 3	- C 4	1.530 (4)
Si5	- Si6	2.356 (1)	C 7	- C 8	1.589 (6)
Si6	- C 7	1.869 (4)	C 8	- C 9	1.500 (6)
Si6	- C 16	1.879 (5)			

Table 8. Intermolecular Distances (Å) with Esd's in Parentheses for **3a₄**

atom	atom	adc	distance	atom	atom	adc	distance
Si1	- Si1	(2)	2.352 (2)	Si10	- Si10	(2)	2.366 (2)

Table 9. Intramolecular Angles (deg) with Esd's in Parentheses for **3a4**

atom	atom	atom	angle	atom	atom	atom	angle
C 12	- Si1	- C 2	108.6 (2)	C 16	- Si6	- C 15	108.6 (2)
C 12	- Si1	- C 11	108.1 (2)	C 16	- Si6	- Si5	107.7 (1)
C 2	- Si1	- C 11	108.8 (2)	C 15	- Si6	- Si5	109.6 (1)
C 14	- Si5	- C 13	108.1 (2)	C 9	- Si10	- C 18	109.2 (2)
C 14	- Si5	- C 4	108.1 (2)	C 9	- Si10	- C 17	106.7 (2)
C 14	- Si5	- Si6	108.5 (2)	C 18	- Si10	- C 17	108.0 (3)
C 13	- Si5	- C 4	109.2 (2)	C 3	- C 2	- Si1	115.6 (2)
C 13	- Si5	- Si6	109.7 (2)	C 4	- C 3	- C 2	115.0 (3)
C 4	- Si5	- Si6	113.0 (1)	C 3	- C 4	- Si5	115.8 (3)
C 7	- Si6	- C 16	109.0 (2)	C 8	- C 7	- Si6	112.7 (2)
C 7	- Si6	- C 15	109.2 (2)	C 9	- C 8	- C 7	115.2 (3)
C 7	- Si6	- Si5	112.6 (1)	C 8	- C 9	- Si10	114.1 (3)

Table 10. Intermolecular Angles (deg) with Esd's in Parentheses for **3a4**

atom	atom	adc	atom	adc	angle	atom	atom	adc	atom	adc	angle
C 12	- Si1	(1)	- Si1	(2)	109.5 (2)	C 9	- Si10	(1)	- Si10	(2)	115.3 (2)
C 2	- Si1	(1)	- Si1	(2)	110.7 (1)	C 18	- Si10	(1)	- Si10	(2)	107.3 (2)
C 11	- Si1	(1)	- Si1	(2)	111.1 (1)	C 17	- Si10	(1)	- Si10	(2)	110.1 (2)

Table 11. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **4b**

atom	x/a	y/b	z/c	U(iso)
Pd1	0.50000	0.21886(11)	0.25000	0.045
Si2	0.5624(2)	0.3721(4)	0.3742(3)	0.065
N 3	0.4105(6)	0.0321(10)	0.0608(10)	0.060
C 4	0.4424(8)	0.0985(13)	0.1283(13)	0.066
C 5	0.3684(7)	-0.0479(12)	-0.0306(11)	0.052
C 6	0.3500(17)	-0.1548(22)	0.0129(22)	0.127
C 7	0.5600(17)	0.3492(25)	0.5020(21)	0.137
C 8	0.6568(12)	0.3504(28)	0.4220(26)	0.136
C 9	0.3483(14)	-0.2740(17)	-0.1340(26)	0.106
C 10	0.4126(11)	-0.0862(22)	-0.0772(21)	0.114
C 11	0.3067(17)	-0.2425(25)	-0.0866(24)	0.123
C 12	0.2607(15)	-0.0691(24)	-0.2121(23)	0.117
C 13	0.3051(12)	0.0170(19)	-0.1130(23)	0.107
C 14	0.3672(13)	-0.1710(22)	-0.1750(21)	0.122
C 15	0.2445(15)	-0.1782(32)	-0.1619(36)	0.165
C 16	0.305(2)	-0.104(3)	-0.257(2)	0.150

C 17	0.549(2)	0.536(2)	0.347(2)	0.163
C 18	0.525(6)	0.575(4)	0.242(9)	0.217
H 6A	0.32278	-0.13141	0.04323	0.2(1)
H 6B	0.39098	-0.19331	0.06823	0.1(1)
H 7A	0.58538	0.41158	0.55255	0.12(8)
H 7B	0.57978	0.27388	0.53425	0.6(6)
H 7C	0.51308	0.35108	0.48435	0.1(1)
H 8A	0.68215	0.41277	0.47258	0.10(7)
H 8B	0.66235	0.35517	0.36038	0.5(4)
H 8C	0.67305	0.27457	0.45648	0.6(5)
H 9A	0.32270	-0.32885	-0.19247	0.3(3)
H 9B	0.38950	-0.31195	-0.07867	0.11(8)
H 10A	0.45259	-0.12792	-0.02300	0.11(9)
H 10B	0.42679	-0.01852	-0.10120	0.12(9)
H 11	0.29399	-0.31253	-0.06306	0.08(6)
H 12	0.21830	-0.03193	-0.26477	0.2(2)
H 13A	0.31832	0.08402	-0.13942	0.09(6)
H 13B	0.27942	0.04452	-0.08142	0.2(2)
H 14	0.39233	-0.19644	-0.20825	0.2(2)
H 15A	0.22479	-0.15056	-0.12083	0.3(2)
H 15B	0.21239	-0.23016	-0.21843	0.3(2)
H 16A	0.31853	-0.03226	-0.27660	0.3(3)
H 16B	0.27803	-0.15146	-0.32020	0.12(8)
H 17A	0.59163	0.57529	0.39455	0.13(9)
H 17B	0.51523	0.56239	0.36395	0.6(6)

T=exp[$-2\pi^2$U], U=U(iso) or [U(11)+U(22)+U(33)]/3

Table 12. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **4b**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Pd1	0.0369(9)	0.0317(9)	0.0396(9)	0.0000	0.0089(6)	0.0000
Si2	0.055(2)	0.044(2)	0.055(2)	-0.011(2)	0.021(2)	-0.012(2)
N 3	0.052(6)	0.044(6)	0.048(6)	-0.007(5)	0.012(5)	-0.011(5)
C 4	0.059(8)	0.040(7)	0.057(8)	0.001(6)	0.023(7)	0.001(6)
C 5	0.038(6)	0.041(6)	0.045(7)	-0.004(5)	0.009(5)	-0.012(5)
C 6	0.13(2)	0.09(1)	0.09(2)	-0.05(2)	0.05(2)	-0.02(1)
C 7	0.14(2)	0.11(2)	0.08(1)	-0.03(2)	0.06(1)	-0.04(1)
C 8	0.06(1)	0.15(2)	0.12(2)	-0.05(1)	0.04(1)	-0.07(2)
C 9	0.08(1)	0.06(1)	0.11(2)	0.00(1)	0.03(1)	-0.02(1)
C 10	0.07(1)	0.10(1)	0.11(2)	-0.02(1)	0.05(1)	-0.04(1)
C 11	0.11(2)	0.08(1)	0.10(2)	-0.04(2)	0.05(2)	-0.02(1)
C 12	0.10(2)	0.09(2)	0.09(2)	0.05(2)	-0.03(1)	-0.02(1)
C 13	0.08(1)	0.07(1)	0.11(2)	0.02(1)	-0.01(1)	-0.03(1)
C 14	0.09(1)	0.10(2)	0.10(2)	-0.02(1)	0.06(1)	-0.04(1)
C 15	0.08(2)	0.12(2)	0.19(3)	-0.04(2)	0.06(2)	-0.07(2)
C 16	0.19(3)	0.10(2)	0.07(1)	-0.05(2)	0.04(2)	-0.02(1)
C 17	0.24(4)	0.04(1)	0.08(2)	-0.02(2)	-0.01(2)	-0.01(1)
C 18	0.3(2)	0.1(0)	0.1(0)	-0.1(1)	0.1(1)	0.0(0)

Table 13. Intramolecular Distances (Å) with Esd's in Parentheses for **4b**

atom	atom	distance	atom	atom	distance
Pd1	- Si2	2.358(5)	Pd1	- C 4	2.059(16)
Si2	- C 7	1.88(3)	Si2	- C 8	1.90(3)
Si2	- C 17	1.89(3)	N 3	- C 4	1.14(2)
N 3	- C 5	1.466(19)	C 5	- C 6	1.51(3)
C 5	- C 10	1.53(3)	C 5	- C 13	1.50(3)
C 6	- C 11	1.59(4)	C 9	- C 11	1.47(5)
C 9	- C 14	1.46(4)	C 10	- C 14	1.56(4)
C 11	- C 15	1.45(5)	C 12	- C 13	1.58(4)
C 12	- C 15	1.56(5)	C 12	- C 16	1.49(5)
C 14	- C 16	1.50(5)	C 17	- C 18	1.56(12)
C 17'	- C 18	1.38(11)			

Table 14. Intramolecular Angles (deg) with Esd's in Parentheses for **4b**

atom	atom	atom	angle	atom	atom	atom	angle
Si2	- Pd1	- Si2'	85.8(2)	Si2	- Pd1	- C 4	173.7(5)
Si2	- Pd1	- C 4'	88.3(5)	C 4	- Pd1	- C 4'	97.6(6)
Pd1	- Si2	- C 8	107.6(10)	Pd1	- Si2	- C 17	126.3(9)
Pd1	- Si2	- C 7	109.1(9)	C 7	- Si2	- C 8	103.3(14)
C 7	- Si2	- C 17	104.7(14)	C 8	- Si2	- C 17	103.6(17)
C 4	- N 3	- C 5	176.7(15)	Pd1	- C 4	- N 3	179.9
N 3	- C 5	- C 6	108.1(15)	N 3	- C 5	- C 10	107.1(14)
N 3	- C 5	- C 13	108.7(14)	C 6	- C 5	- C 10	110.0(17)
C 6	- C 5	- C 13	110.9(17)	C 10	- C 5	- C 13	111.9(17)
C 5	- C 6	- C 11	107.3(21)	C 11	- C 9	- C 14	113.0(20)
C 5	- C 10	- C 14	106.8(17)	C 6	- C 11	- C 9	108.6(25)
C 6	- C 11	- C 15	105.6(26)	C 9	- C 11	- C 15	112.8(27)
C 13	- C 12	- C 15	105.1(25)	C 13	- C 12	- C 16	106.7(23)
C 15	- C 12	- C 16	111.4(25)	C 5	- C 13	- C 12	108.4(18)
C 9	- C 14	- C 10	108.5(22)	C 9	- C 14	- C 16	111.0(25)
C 10	- C 14	- C 16	108.0(21)	C 11	- C 15	- C 12	111.4(26)
C 12	- C 16	- C 14	111.9(23)	Si2	- C 17	- C 18	116.0(27)
Si2'	- C 17'	- C 18	117.8(28)	C 17	- C 18	- C 17'	116.5(70)

Table 15. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **11a**

atom	x	y	z	B(eq)
Si1	-0.04177 (5)	0.0197600	-0.38046 (7)	4.58 (4)
Si5	0.15898 (5)	0.17235 (5)	-0.48921 (7)	4.22 (4)
Si7	0.17742 (5)	0.27821 (5)	-0.35031 (6)	3.83 (4)
Si11	0.37317 (5)	0.14644 (5)	-0.16122 (7)	4.80 (4)
Si13	0.32419 (5)	0.02556 (5)	-0.12146 (8)	5.24 (4)
Si17	0.09899 (5)	-0.05880 (5)	-0.34947 (7)	4.56 (4)
N 31	0.0053 (2)	-0.0441 (1)	-0.5123 (2)	4.59 (8)
N 32	0.2374 (1)	0.2500 (1)	-0.5351 (2)	4.27 (8)
N 33	0.3918 (2)	0.0822 (1)	0.0053 (2)	4.66 (8)
C 2	0.0060 (2)	0.0795 (1)	-0.3484 (3)	5.5 (1)
C 3	0.0524 (2)	0.1018 (1)	-0.4287 (3)	5.0 (1)
C 4	0.0937 (2)	0.1492 (2)	-0.3979 (3)	5.5 (1)
C 6	0.1975 (2)	0.2387 (1)	-0.4634 (2)	3.78 (8)
C 8	0.1940 (2)	0.2351 (2)	-0.2451 (3)	4.5 (1)
C 9	0.2684 (2)	0.2130 (2)	-0.2428 (3)	5.2 (1)
C 10	0.2802 (2)	0.1723 (2)	-0.1668 (3)	5.1 (1)
C 12	0.3679 (2)	0.0876 (1)	-0.0805 (3)	4.34 (9)
C 14	0.2566 (3)	0.0341 (2)	-0.2185 (4)	7.3 (2)
C 15	0.2155 (2)	-0.0139 (2)	-0.2447 (4)	6.1 (1)
C 16	0.1576 (3)	-0.0043 (2)	-0.3198 (4)	7.4 (2)
C 18	0.0224 (2)	-0.0313 (1)	-0.4263 (2)	3.94 (9)
C 19	-0.1059 (3)	0.0329 (2)	-0.4784 (5)	7.7 (2)
C 20	-0.0910 (3)	-0.0049 (2)	-0.2734 (5)	7.8 (2)
C 21	0.1159 (3)	0.1768 (2)	-0.6098 (4)	7.2 (2)
C 22	0.2349 (3)	0.1272 (2)	-0.4929 (5)	6.9 (2)
C 23	0.0820 (2)	0.2965 (2)	-0.3560 (4)	5.4 (1)
C 24	0.2321 (2)	0.3367 (2)	-0.3323 (3)	5.2 (1)
C 25	0.4032 (3)	0.1238 (2)	-0.2815 (3)	6.5 (1)
C 26	0.4336 (3)	0.1987 (2)	-0.1224 (5)	7.6 (2)
C 27	0.2792 (4)	-0.0013 (2)	-0.0150 (5)	8.7 (2)
C 28	0.3950 (3)	-0.0174 (2)	-0.1628 (6)	9.2 (2)
C 29	0.0592 (4)	-0.0844 (3)	-0.2370 (5)	9.7 (2)
C 30	0.1526 (4)	-0.1103 (3)	-0.4031 (6)	11.1 (3)
C 34	0.0403 (2)	-0.0833 (1)	-0.5653 (3)	5.0 (1)
C 35	0.0101 (2)	-0.1318 (2)	-0.5644 (3)	5.6 (1)
C 36	0.0442 (3)	-0.1685 (2)	-0.6209 (4)	8.1 (2)
C 37	0.1022 (4)	-0.1569 (2)	-0.6762 (4)	9.2 (2)
C 38	0.1287 (3)	-0.1093 (2)	-0.6774 (4)	8.2 (2)
C 39	0.0988 (2)	-0.0708 (2)	-0.6223 (3)	6.0 (1)
C 40	-0.0553 (3)	-0.1430 (2)	-0.5077 (4)	6.5 (1)
C 41	-0.0640 (5)	-0.1976 (2)	-0.4758 (6)	11.1 (3)
C 42	-0.1201 (4)	-0.1252 (4)	-0.5632 (7)	11.2 (3)
C 43	0.1266 (3)	-0.0166 (2)	-0.6275 (4)	7.2 (2)
C 44	0.2048 (5)	-0.0141 (4)	-0.6543 (9)	13.0 (4)
C 45	0.0834 (6)	0.0142 (4)	-0.6935 (8)	12.2 (3)
C 46	0.2736 (2)	0.2974 (1)	-0.5426 (2)	4.27 (9)
C 47	0.2384 (2)	0.3382 (1)	-0.5865 (3)	5.1 (1)
C 48	0.2770 (3)	0.3832 (2)	-0.5969 (3)	6.1 (1)
C 49	0.3448 (3)	0.3873 (2)	-0.5666 (4)	6.8 (1)
C 50	0.3794 (2)	0.3463 (2)	-0.5254 (3)	6.1 (1)
C 51	0.3441 (2)	0.3007 (1)	-0.5132 (2)	4.7 (1)
C 52	0.1628 (3)	0.3337 (2)	-0.6230 (4)	6.8 (1)

C 53	0.1590 (6)	0.3257 (5)	-0.7302 (6)	15.0 (5)
C 54	0.1159 (4)	0.3783 (2)	-0.5926 (6)	9.0 (2)
C 55	0.3804 (2)	0.2548 (2)	-0.4697 (3)	5.6 (1)
C 56	0.4036 (3)	0.2180 (2)	-0.5491 (5)	7.8 (2)
C 57	0.4428 (3)	0.2682 (3)	-0.4044 (5)	8.2 (2)
C 58	0.4293 (2)	0.1209 (1)	0.0559 (2)	4.49 (9)
C 59	0.5040 (2)	0.1216 (2)	0.0488 (3)	5.2 (1)
C 60	0.5398 (2)	0.1576 (2)	0.1045 (3)	6.0 (1)
C 61	0.5038 (3)	0.1907 (2)	0.1629 (3)	6.6 (1)
C 62	0.4317 (3)	0.1891 (2)	0.1682 (3)	6.1 (1)
C 63	0.3915 (2)	0.1542 (2)	0.1153 (3)	5.1 (1)
C 64	0.5431 (2)	0.0849 (2)	-0.0141 (4)	6.6 (1)
C 65	0.5511 (4)	0.0344 (3)	0.0356 (6)	10.0 (2)
C 66	0.6142 (4)	0.1042 (4)	-0.0512 (6)	10.6 (3)
C 67	0.3122 (2)	0.1519 (2)	0.1244 (3)	6.4 (1)
C 68	0.2778 (4)	0.2039 (3)	0.1340 (7)	11.2 (3)
C 69	0.2903 (4)	0.1151 (4)	0.2028 (6)	10.6 (3)
H 48	0.253 (3)	0.410 (2)	-0.622 (4)	6.06 (0)
H 3A	0.090 (2)	0.076 (2)	-0.450 (3)	5.00 (0)
H 9A	0.297 (3)	0.234 (2)	-0.239 (4)	5.23 (0)
H 24A	0.284 (3)	0.329 (2)	-0.330 (3)	5.19 (0)
H 62	0.408 (3)	0.210 (2)	0.211 (4)	6.12 (0)
H 3B	0.019 (2)	0.110 (2)	-0.490 (3)	5.00 (0)
H 24B	0.230 (2)	0.360 (2)	-0.385 (4)	5.19 (0)
H 67	0.297 (3)	0.137 (2)	0.072 (4)	6.40 (0)
H 49	0.361 (3)	0.420 (2)	-0.571 (4)	6.80 (0)
H 8A	0.185 (2)	0.254 (2)	-0.186 (3)	4.51 (0)
H 52	0.138 (3)	0.303 (2)	-0.588 (4)	6.83 (0)
H 26A	0.486 (3)	0.185 (2)	-0.122 (4)	7.62 (0)
H 60	0.587 (3)	0.162 (2)	0.100 (4)	6.00 (0)
H 40	-0.049 (3)	-0.128 (2)	-0.448 (4)	6.52 (0)
H 21A	0.144 (3)	0.189 (2)	-0.645 (4)	7.25 (0)
H 24C	0.217 (2)	0.350 (2)	-0.271 (4)	5.19 (0)
H 8B	0.166 (2)	0.209 (2)	-0.245 (3)	4.51 (0)
H 19A	-0.139 (3)	0.053 (2)	-0.461 (4)	7.72 (0)
H 4A	0.062 (2)	0.176 (2)	-0.382 (3)	5.46 (0)
H 50	0.430 (3)	0.353 (2)	-0.498 (4)	6.09 (0)
H 26B	0.423 (3)	0.214 (2)	-0.057 (5)	7.62 (0)
H 4B	0.125 (3)	0.140 (2)	-0.343 (4)	5.46 (0)
H 61	0.536 (3)	0.216 (2)	0.203 (4)	6.56 (0)
H 2A	-0.025 (3)	0.099 (2)	-0.330 (4)	5.51 (0)
H 19B	-0.136 (3)	-0.003 (2)	-0.490 (4)	7.72 (0)
H 69A	0.236 (4)	0.110 (3)	0.203 (5)	10.60 (0)
H 19C	-0.080 (3)	0.045 (2)	-0.541 (5)	7.72 (0)
H 57A	0.485 (3)	0.287 (2)	-0.443 (4)	8.25 (0)
H 23A	0.052 (3)	0.267 (2)	-0.356 (4)	5.46 (0)
H 26C	0.439 (3)	0.219 (2)	-0.169 (4)	7.62 (0)
H 2B	0.034 (2)	0.071 (2)	-0.290 (4)	5.51 (0)
H 43	0.125 (3)	-0.006 (2)	-0.560 (5)	7.24 (0)
H 36	0.018 (3)	-0.202 (2)	-0.620 (4)	8.12 (0)
H 41A	-0.068 (4)	-0.213 (3)	-0.535 (6)	11.13 (0)
H 25A	0.456 (3)	0.115 (2)	-0.283 (4)	6.50 (0)
H 55	0.338 (2)	0.237 (2)	-0.433 (4)	5.56 (0)
H 28A	0.378 (3)	-0.051 (3)	-0.178 (5)	9.17 (0)
H 14A	0.221 (3)	0.057 (2)	-0.202 (5)	7.27 (0)
H 38	0.166 (3)	-0.101 (2)	-0.722 (5)	8.21 (0)
H 21B	0.105 (3)	0.148 (3)	-0.624 (4)	7.25 (0)
H 69B	0.293 (5)	0.140 (3)	0.261 (8)	10.60 (0)
H 22A	0.276 (3)	0.138 (2)	-0.534 (4)	6.87 (0)
H 10A	0.242 (2)	0.144 (2)	-0.185 (3)	5.08 (0)
H 22B	0.257 (3)	0.121 (2)	-0.419 (4)	6.87 (0)

H 66A	0.601 (4)	0.132 (3)	-0.088 (6)	10.63 (0)
H 15A	0.195 (3)	-0.026 (2)	-0.181 (4)	6.06 (0)
H 54A	0.129 (4)	0.407 (3)	-0.628 (5)	8.99 (0)
H 28B	0.422 (4)	-0.017 (3)	-0.113 (5)	9.17 (0)
H 65A	0.568 (4)	0.010 (3)	-0.018 (6)	9.97 (0)
H 15B	0.248 (3)	-0.038 (2)	-0.272 (4)	6.06 (0)
H 20A	-0.127 (3)	0.019 (3)	-0.263 (4)	7.76 (0)
H 14B	0.274 (3)	0.049 (2)	-0.273 (4)	7.27 (0)
H 37	0.131 (4)	-0.188 (2)	-0.707 (5)	9.21 (0)
H 27A	0.243 (4)	-0.032 (2)	-0.025 (4)	8.68 (0)
H 29A	0.092 (4)	-0.094 (3)	-0.200 (5)	9.66 (0)
H 9B	0.284 (2)	0.196 (2)	-0.315 (4)	5.23 (0)
H 25B	0.411 (3)	0.159 (2)	-0.326 (4)	6.50 (0)
H 44A	0.214 (5)	0.018 (4)	-0.649 (7)	12.96 (0)
H 20B	-0.064 (3)	0.001 (2)	-0.220 (5)	7.76 (0)
H 56A	0.428 (3)	0.186 (2)	-0.524 (4)	7.77 (0)
H 27B	0.299 (4)	-0.000 (3)	0.036 (5)	8.68 (0)
H 56B	0.360 (3)	0.205 (2)	-0.593 (4)	7.77 (0)
H 65B	0.586 (4)	0.045 (3)	0.100 (6)	9.97 (0)
H 44B	0.232 (5)	-0.032 (4)	-0.608 (8)	12.96 (0)
H 45A	0.092 (5)	0.003 (4)	-0.759 (7)	12.23 (0)
H 22C	0.224 (3)	0.098 (2)	-0.504 (4)	6.87 (0)
H 57B	0.433 (4)	0.291 (3)	-0.357 (5)	8.25 (0)
H 44C	0.201 (4)	-0.020 (3)	-0.741 (7)	12.96 (0)
H 45B	0.097 (5)	0.049 (4)	-0.696 (7)	12.23 (0)
H 30A	0.186 (4)	-0.119 (3)	-0.348 (6)	11.10 (0)
H 23B	0.072 (2)	0.320 (2)	-0.412 (4)	5.46 (0)
H 23C	0.069 (3)	0.308 (2)	-0.297 (4)	5.46 (0)
H 29B	0.041 (3)	-0.040 (3)	-0.199 (5)	9.66 (0)
H 64	0.512 (3)	0.081 (2)	-0.073 (4)	6.59 (0)
H 45C	0.040 (5)	0.018 (4)	-0.677 (8)	12.23 (0)
H 25C	0.373 (3)	0.099 (2)	-0.309 (4)	6.50 (0)
H 10B	0.266 (2)	0.182 (2)	-0.109 (4)	5.08 (0)
H 42A	-0.107 (4)	-0.080 (3)	-0.579 (6)	11.15 (0)
H 41B	-0.017 (4)	-0.207 (3)	-0.450 (6)	11.13 (0)
H 20C	-0.109 (3)	-0.037 (2)	-0.285 (4)	7.76 (0)
H 66B	0.633 (4)	0.079 (3)	-0.103 (6)	10.63 (0)
H 41C	-0.106 (4)	-0.203 (3)	-0.430 (6)	11.13 (0)
H 54B	0.064 (4)	0.367 (3)	-0.612 (5)	8.99 (0)
H 57C	0.463 (3)	0.229 (2)	-0.378 (4)	8.25 (0)
H 16A	0.178 (3)	0.010 (2)	-0.376 (4)	7.47 (0)
H 28C	0.418 (4)	-0.004 (3)	-0.223 (5)	9.17 (0)
H 16B	0.125 (3)	0.027 (2)	-0.286 (4)	7.47 (0)
H 65C	0.493 (4)	0.022 (3)	0.058 (5)	9.97 (0)
H 66C	0.652 (4)	0.095 (3)	0.019 (6)	10.63 (0)
H 29C	0.018 (4)	-0.113 (3)	-0.244 (5)	9.66 (0)
H 53A	0.186 (6)	0.351 (5)	-0.760 (8)	15.06 (0)
H 30B	0.120 (4)	-0.128 (3)	-0.425 (7)	11.10 (0)
H 30C	0.178 (4)	-0.118 (3)	-0.464 (6)	11.10 (0)
H 56C	0.439 (3)	0.233 (2)	-0.586 (5)	7.77 (0)
H 42B	-0.129 (4)	-0.154 (3)	-0.619 (6)	11.15 (0)
H 68A	0.293 (5)	0.216 (4)	0.184 (7)	11.17 (0)
H 27C	0.250 (4)	0.025 (3)	0.018 (5)	8.68 (0)
H 42C	-0.170 (4)	-0.129 (3)	-0.527 (5)	11.15 (0)
H 53B	0.186 (6)	0.295 (4)	-0.735 (8)	15.06 (0)
H 69C	0.314 (4)	0.119 (3)	0.263 (8)	10.60 (0)
H 54C	0.116 (3)	0.386 (3)	-0.509 (5)	8.99 (0)
H 68B	0.219 (4)	0.191 (3)	0.138 (6)	11.17 (0)
H 68C	0.245 (5)	0.224 (3)	0.096 (6)	11.17 (0)

Table 16. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **11a**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Si1	0.0535 (9)	0.0440 (4)	0.076 (1)	-0.0029 (4)	0.0109 (5)	-0.0006 (5)
Si5	0.0515 (9)	0.0426 (4)	0.066 (1)	-0.0014 (4)	0.0028 (4)	-0.0052 (5)
Si7	0.0537 (9)	0.0440 (4)	0.048 (1)	-0.0002 (4)	-0.0006 (4)	0.0021 (4)
Si11	0.0667 (9)	0.0574 (4)	0.058 (1)	-0.0092 (5)	-0.0165 (5)	0.0115 (5)
Si13	0.0656 (9)	0.0550 (4)	0.078 (1)	-0.0108 (5)	-0.0224 (5)	0.0058 (5)
Si17	0.0578 (9)	0.0542 (4)	0.061 (1)	-0.0018 (4)	-0.0135 (4)	-0.0047 (5)
N 31	0.056 (2)	0.057 (2)	0.061 (2)	-0.000 (1)	-0.007 (1)	-0.007 (1)
N 32	0.058 (2)	0.048 (1)	0.056 (2)	-0.003 (1)	0.005 (1)	0.000 (1)
N 33	0.062 (2)	0.054 (1)	0.061 (2)	-0.004 (1)	-0.013 (1)	0.008 (1)
C 2	0.069 (2)	0.049 (2)	0.091 (3)	-0.006 (2)	0.022 (2)	-0.011 (2)
C 3	0.066 (2)	0.046 (2)	0.078 (3)	-0.011 (2)	0.009 (2)	-0.005 (2)
C 4	0.075 (2)	0.047 (2)	0.085 (3)	-0.012 (2)	0.016 (2)	-0.012 (2)
C 6	0.048 (2)	0.044 (1)	0.052 (2)	0.001 (1)	-0.001 (1)	0.003 (1)
C 8	0.066 (2)	0.054 (2)	0.051 (2)	-0.001 (2)	-0.000 (2)	0.005 (2)
C 9	0.067 (2)	0.070 (2)	0.062 (2)	-0.001 (2)	-0.004 (2)	0.021 (2)
C 10	0.075 (2)	0.060 (2)	0.058 (2)	0.002 (2)	-0.009 (2)	0.012 (2)
C 12	0.052 (2)	0.056 (2)	0.056 (2)	-0.003 (2)	-0.012 (2)	0.010 (2)
C 14	0.099 (3)	0.068 (3)	0.109 (4)	-0.026 (2)	-0.053 (3)	0.014 (2)
C 15	0.074 (2)	0.064 (2)	0.092 (3)	-0.011 (2)	-0.031 (2)	-0.002 (2)
C 16	0.095 (3)	0.077 (3)	0.111 (4)	-0.025 (2)	-0.052 (3)	0.016 (3)
C 18	0.053 (2)	0.045 (2)	0.052 (2)	-0.007 (1)	0.000 (2)	-0.007 (1)
C 19	0.076 (3)	0.076 (3)	0.140 (5)	0.023 (2)	-0.012 (3)	0.005 (3)
C 20	0.103 (4)	0.078 (3)	0.113 (4)	-0.001 (3)	0.042 (3)	0.006 (3)
C 21	0.108 (4)	0.086 (3)	0.081 (3)	-0.031 (3)	-0.018 (2)	-0.001 (3)
C 22	0.073 (3)	0.049 (2)	0.139 (4)	0.009 (2)	0.015 (3)	-0.002 (2)
C 23	0.066 (2)	0.069 (2)	0.072 (3)	0.009 (2)	0.001 (2)	0.001 (2)
C 24	0.082 (3)	0.058 (2)	0.056 (2)	-0.012 (2)	0.006 (2)	-0.005 (2)
C 25	0.079 (3)	0.093 (3)	0.075 (3)	-0.008 (2)	0.006 (2)	0.012 (2)
C 26	0.114 (4)	0.074 (3)	0.101 (4)	-0.038 (3)	-0.036 (3)	0.030 (3)
C 27	0.132 (5)	0.100 (4)	0.098 (4)	-0.047 (4)	-0.014 (3)	0.018 (3)
C 28	0.101 (4)	0.086 (4)	0.161 (6)	0.008 (3)	-0.023 (4)	-0.038 (4)
C 29	0.105 (4)	0.151 (6)	0.111 (5)	-0.006 (4)	-0.011 (3)	0.067 (4)
C 30	0.136 (5)	0.155 (6)	0.130 (5)	0.085 (5)	-0.070 (4)	-0.062 (5)
C 34	0.071 (2)	0.064 (2)	0.055 (2)	0.002 (2)	-0.010 (2)	-0.012 (2)
C 35	0.082 (3)	0.068 (2)	0.064 (2)	0.002 (2)	-0.006 (2)	-0.019 (2)
C 36	0.134 (4)	0.075 (3)	0.099 (4)	-0.011 (3)	0.012 (3)	-0.035 (3)
C 37	0.138 (5)	0.100 (4)	0.112 (4)	0.004 (4)	0.040 (4)	-0.043 (3)
C 38	0.121 (4)	0.097 (4)	0.094 (4)	-0.007 (3)	0.036 (3)	-0.031 (3)
C 39	0.076 (2)	0.086 (3)	0.067 (3)	-0.005 (2)	0.008 (2)	-0.022 (2)
C 40	0.091 (3)	0.069 (2)	0.087 (3)	-0.013 (2)	-0.003 (2)	-0.016 (2)
C 41	0.194 (8)	0.080 (4)	0.149 (7)	-0.014 (4)	0.056 (6)	0.004 (4)
C 42	0.086 (4)	0.154 (6)	0.184 (8)	-0.016 (4)	-0.024 (4)	0.006 (6)
C 43	0.099 (3)	0.091 (3)	0.084 (3)	-0.017 (3)	0.017 (3)	-0.016 (3)
C 44	0.131 (6)	0.149 (8)	0.21 (1)	-0.044 (6)	0.066 (6)	-0.048 (7)
C 45	0.188 (8)	0.120 (6)	0.156 (7)	-0.030 (6)	-0.018 (7)	0.028 (6)
C 46	0.066 (2)	0.049 (2)	0.047 (2)	-0.005 (2)	0.012 (2)	-0.001 (1)
C 47	0.086 (3)	0.053 (2)	0.054 (2)	-0.003 (2)	0.002 (2)	0.004 (2)
C 48	0.105 (4)	0.056 (2)	0.069 (3)	-0.002 (2)	0.012 (2)	0.010 (2)
C 49	0.104 (4)	0.064 (2)	0.090 (3)	-0.024 (2)	0.023 (3)	0.006 (2)
C 50	0.077 (3)	0.068 (2)	0.086 (3)	-0.018 (2)	0.020 (2)	-0.000 (2)
C 51	0.063 (2)	0.062 (2)	0.056 (2)	-0.010 (2)	0.014 (2)	-0.001 (2)

C 52	0.102 (3)	0.072 (3)	0.086 (3)	0.006 (2)	-0.022 (2)	0.014 (2)
C 53	0.19 (1)	0.27 (2)	0.109 (6)	0.021 (8)	-0.041 (6)	-0.064 (8)
C 54	0.102 (4)	0.100 (4)	0.139 (6)	0.016 (3)	-0.028 (4)	0.024 (4)
C 55	0.054 (2)	0.070 (2)	0.087 (3)	-0.001 (2)	0.010 (2)	0.006 (2)
C 56	0.086 (3)	0.087 (3)	0.122 (4)	0.010 (3)	0.027 (3)	-0.008 (3)
C 57	0.077 (3)	0.114 (4)	0.122 (5)	-0.002 (3)	-0.016 (3)	0.011 (4)
C 58	0.068 (2)	0.054 (2)	0.048 (2)	-0.007 (2)	-0.018 (2)	0.012 (2)
C 59	0.068 (2)	0.070 (2)	0.059 (2)	-0.006 (2)	-0.019 (2)	0.013 (2)
C 60	0.076 (2)	0.081 (3)	0.071 (3)	-0.015 (2)	-0.029 (2)	0.007 (2)
C 61	0.102 (4)	0.071 (2)	0.076 (3)	-0.010 (2)	-0.039 (2)	0.002 (2)
C 62	0.104 (4)	0.068 (2)	0.060 (3)	0.006 (2)	-0.017 (2)	-0.000 (2)
C 63	0.078 (2)	0.059 (2)	0.055 (2)	-0.001 (2)	-0.012 (2)	0.006 (2)
C 64	0.063 (2)	0.098 (3)	0.090 (3)	-0.003 (2)	-0.011 (2)	-0.008 (3)
C 65	0.128 (5)	0.101 (4)	0.149 (6)	0.032 (4)	-0.001 (5)	-0.002 (4)
C 66	0.097 (4)	0.163 (7)	0.144 (7)	-0.012 (4)	0.021 (4)	-0.005 (5)
C 67	0.082 (3)	0.090 (3)	0.071 (3)	0.008 (2)	-0.008 (2)	-0.002 (2)
C 68	0.109 (5)	0.122 (6)	0.193 (9)	0.043 (4)	-0.021 (5)	-0.012 (5)
C 69	0.099 (4)	0.194 (8)	0.110 (5)	-0.011 (5)	0.004 (4)	0.058 (6)

Table 17. Intramolecular Distances (Å) with Esd's in Parentheses for **11a**

atom	atom	distance	atom	atom	distance
Si1	- C 19	1.853 (6)	C 34	- C 39	1.396 (6)
Si1	- C 20	1.869 (6)	C 34	- C 35	1.400 (5)
Si1	- C 2	1.870 (4)	C 35	- C 36	1.404 (7)
Si1	- C 18	1.919 (3)	C 35	- C 40	1.493 (6)
Si5	- C 22	1.862 (5)	C 36	- C 37	1.371 (9)
Si5	- C 21	1.866 (6)	C 37	- C 38	1.352 (9)
Si5	- C 4	1.870 (4)	C 38	- C 39	1.391 (7)
Si5	- C 6	1.927 (3)	C 39	- C 43	1.524 (7)
Si7	- C 23	1.866 (4)	C 40	- C 41	1.517 (8)
Si7	- C 24	1.872 (4)	C 40	- C 42	1.519 (9)
Si7	- C 8	1.878 (4)	C 43	- C 45	1.47 (1)
Si7	- C 6	1.923 (3)	C 43	- C 44	1.52 (1)
Si11	- C 25	1.862 (5)	C 46	- C 51	1.393 (5)
Si11	- C 26	1.867 (6)	C 46	- C 47	1.403 (5)
Si11	- C 10	1.883 (4)	C 47	- C 48	1.399 (6)
Si11	- C 12	1.917 (4)	C 47	- C 52	1.518 (6)
Si13	- C 28	1.843 (7)	C 48	- C 49	1.351 (8)
Si13	- C 27	1.846 (7)	C 49	- C 50	1.386 (7)
Si13	- C 14	1.868 (6)	C 50	- C 51	1.384 (6)
Si13	- C 12	1.919 (4)	C 51	- C 55	1.517 (6)
Si17	- C 30	1.849 (8)	C 52	- C 53	1.50 (1)
Si17	- C 29	1.859 (7)	C 52	- C 54	1.530 (8)
Si17	- C 16	1.859 (6)	C 55	- C 57	1.527 (7)
Si17	- C 18	1.936 (3)	C 55	- C 56	1.532 (8)
N 31	- C 18	1.283 (4)	C 58	- C 63	1.400 (5)
N 31	- C 34	1.430 (5)	C 58	- C 59	1.412 (5)
N 32	- C 6	1.283 (4)	C 59	- C 60	1.398 (6)
N 32	- C 46	1.428 (4)	C 59	- C 64	1.497 (6)
N 33	- C 12	1.282 (4)	C 60	- C 61	1.372 (7)
N 33	- C 58	1.428 (4)	C 61	- C 62	1.362 (7)
C 2	- C 3	1.534 (6)	C 62	- C 63	1.400 (6)

C 3	- C 4	1.533 (6)	C 63	- C 67	1.503 (6)
C 8	- C 9	1.520 (6)	C 64	- C 65	1.509 (9)
C 9	- C 10	1.521 (6)	C 64	- C 66	1.525 (9)
C 14	- C 15	1.530 (7)	C 67	- C 69	1.52 (1)
C 15	- C 16	1.532 (8)	C 67	- C 68	1.52 (1)

Table 18. Intramolecular Angles (deg) with Esd's in Parentheses for **11a**

atom	atom	atom	angle	atom	atom	atom	angle
C 19	- Si1	- C 20	109.0 (3)	Si1	- C 18	- Si17	123.4 (2)
C 19	- Si1	- C 2	109.4 (2)	C 39	- C 34	- C 35	122.8 (4)
C 19	- Si1	- C 18	107.4 (2)	C 39	- C 34	- N 31	119.1 (3)
C 20	- Si1	- C 2	110.0 (2)	C 35	- C 34	- N 31	117.8 (3)
C 20	- Si1	- C 18	109.4 (2)	C 34	- C 35	- C 36	116.1 (4)
C 2	- Si1	- C 18	111.5 (2)	C 34	- C 35	- C 40	121.5 (4)
C 22	- Si5	- C 21	110.5 (3)	C 36	- C 35	- C 40	122.4 (4)
C 22	- Si5	- C 4	108.4 (2)	C 37	- C 36	- C 35	121.5 (5)
C 22	- Si5	- C 6	107.2 (2)	C 38	- C 37	- C 36	120.7 (6)
C 21	- Si5	- C 4	110.0 (2)	C 37	- C 38	- C 39	121.4 (5)
C 21	- Si5	- C 6	105.9 (2)	C 38	- C 39	- C 34	117.4 (4)
C 4	- Si5	- C 6	114.8 (2)	C 38	- C 39	- C 43	121.2 (4)
C 23	- Si7	- C 24	109.0 (2)	C 34	- C 39	- C 43	121.3 (4)
C 23	- Si7	- C 8	110.5 (2)	C 35	- C 40	- C 41	115.6 (5)
C 23	- Si7	- C 6	107.2 (2)	C 35	- C 40	- C 42	109.6 (5)
C 24	- Si7	- C 8	107.6 (2)	C 41	- C 40	- C 42	110.8 (6)
C 24	- Si7	- C 6	116.6 (2)	C 45	- C 43	- C 44	111.1 (7)
C 8	- Si7	- C 6	105.9 (2)	C 45	- C 43	- C 39	110.9 (6)
C 25	- Si11	- C 26	108.0 (3)	C 44	- C 43	- C 39	112.6 (5)
C 25	- Si11	- C 10	111.2 (2)	C 51	- C 46	- C 47	122.0 (3)
C 25	- Si11	- C 12	106.3 (2)	C 51	- C 46	- N 32	119.3 (3)
C 26	- Si11	- C 10	108.2 (2)	C 47	- C 46	- N 32	118.5 (3)
C 26	- Si11	- C 12	117.4 (2)	C 48	- C 47	- C 46	116.6 (4)
C 10	- Si11	- C 12	105.6 (2)	C 48	- C 47	- C 52	121.4 (4)
C 28	- Si13	- C 27	110.3 (3)	C 46	- C 47	- C 52	122.0 (3)
C 28	- Si13	- C 14	110.1 (3)	C 49	- C 48	- C 47	121.9 (4)
C 28	- Si13	- C 12	107.8 (2)	C 48	- C 49	- C 50	120.8 (4)
C 27	- Si13	- C 14	108.0 (3)	C 51	- C 50	- C 49	120.0 (4)
C 27	- Si13	- C 12	106.7 (2)	C 50	- C 51	- C 46	118.5 (4)
C 14	- Si13	- C 12	113.8 (2)	C 50	- C 51	- C 55	121.6 (3)
C 30	- Si17	- C 29	107.0 (4)	C 46	- C 51	- C 55	119.9 (3)
C 30	- Si17	- C 16	109.4 (3)	C 53	- C 52	- C 47	112.7 (6)
C 30	- Si17	- C 18	117.4 (3)	C 53	- C 52	- C 54	110.7 (6)
C 29	- Si17	- C 16	109.6 (3)	C 47	- C 52	- C 54	113.0 (4)
C 29	- Si17	- C 18	107.3 (2)	C 51	- C 55	- C 57	113.6 (4)
C 16	- Si17	- C 18	106.0 (2)	C 51	- C 55	- C 56	110.3 (4)
C 18	- N 31	- C 34	123.7 (3)	C 57	- C 55	- C 56	110.7 (4)
C 6	- N 32	- C 46	122.7 (3)	C 63	- C 58	- C 59	122.8 (3)
C 12	- N 33	- C 58	123.4 (3)	C 63	- C 58	- N 33	119.1 (3)
C 3	- C 2	- Si1	115.1 (3)	C 59	- C 58	- N 33	118.0 (3)
C 4	- C 3	- C 2	113.5 (3)	C 60	- C 59	- C 58	116.8 (4)
C 3	- C 4	- Si5	114.3 (3)	C 60	- C 59	- C 64	121.6 (4)
N 32	- C 6	- Si7	128.5 (2)	C 58	- C 59	- C 64	121.6 (3)
N 32	- C 6	- Si5	106.8 (2)	C 61	- C 60	- C 59	121.4 (4)

Si7	- C 6	- Si5	124.7 (2)	C 62	- C 61	- C 60	120.4 (4)
C 9	- C 8	- Si7	113.7 (3)	C 61	- C 62	- C 63	122.2 (4)
C 8	- C 9	- C 10	114.8 (3)	C 62	- C 63	- C 58	116.4 (4)
C 9	- C 10	- Si11	114.8 (3)	C 62	- C 63	- C 67	121.4 (4)
N 33	- C 12	- Si11	128.0 (3)	C 58	- C 63	- C 67	122.1 (4)
N 33	- C 12	- Si13	109.3 (2)	C 59	- C 64	- C 65	110.7 (5)
Si11	- C 12	- Si13	122.6 (2)	C 59	- C 64	- C 66	114.5 (5)
C 15	- C 14	- Si13	114.6 (3)	C 65	- C 64	- C 66	111.2 (5)
C 14	- C 15	- C 16	112.7 (4)	C 63	- C 67	- C 69	110.9 (4)
C 15	- C 16	- Si17	116.5 (4)	C 63	- C 67	- C 68	113.3 (5)
N 31	- C 18	- Si1	109.6 (2)	C 69	- C 67	- C 68	113.4 (6)
N 31	- C 18	- Si17	127.0 (2)				

Table 19. Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2$) with Esd's in Parentheses for **11b**

atom	x	y	z	B(eq)
Si1	-0.16159 (4)	-0.60110 (6)	-0.30091 (4)	5.35 (2)
Si5	-0.23719 (4)	-0.50670 (5)	-0.00819 (4)	5.10 (2)
Si7	-0.14894 (4)	-0.43030 (5)	0.14932 (4)	4.66 (2)
Si11	0.02848 (4)	-0.33321 (6)	0.40717 (4)	5.30 (2)
N 21	-0.1932 (1)	-0.6234 (2)	0.0976 (1)	4.41 (6)
N 22	0.1251 (1)	-0.2179 (2)	0.3246 (1)	4.39 (6)
C 2	-0.1468 (2)	-0.6161 (2)	-0.1996 (2)	5.99 (9)
C 3	-0.1963 (2)	-0.5571 (2)	-0.1535 (1)	5.96 (9)
C 4	-0.1776 (2)	-0.5689 (2)	-0.0713 (2)	6.16 (9)
C 6	-0.1918 (1)	-0.5304 (2)	0.0873 (1)	4.10 (7)
C 8	-0.1048 (2)	-0.4723 (2)	0.2391 (1)	5.28 (9)
C 9	-0.0630 (2)	-0.3914 (2)	0.2819 (1)	5.44 (8)
C 10	-0.0316 (2)	-0.4251 (2)	0.3575 (2)	5.62 (9)
C 12	0.1029 (1)	-0.3026 (2)	0.3440 (1)	4.18 (7)
C 13	-0.2564 (2)	-0.6282 (3)	-0.3333 (2)	7.7 (1)
C 14	-0.1420 (3)	-0.4719 (3)	-0.3258 (2)	8.9 (2)
C 15	-0.3280 (2)	-0.5639 (4)	-0.0118 (2)	8.6 (1)
C 16	-0.2458 (2)	-0.3753 (3)	-0.0336 (2)	8.5 (1)
C 17	-0.2210 (2)	-0.3416 (3)	0.1668 (2)	7.4 (1)
C 18	-0.0812 (2)	-0.3693 (3)	0.0952 (2)	7.0 (1)
C 19	0.0754 (2)	-0.3888 (3)	0.4907 (2)	8.9 (1)
C 20	-0.0296 (2)	-0.2306 (3)	0.4346 (2)	7.9 (1)
C 23	-0.1619 (1)	-0.6708 (2)	0.1613 (1)	4.33 (7)
C 24	-0.2016 (1)	-0.6811 (2)	0.2226 (1)	5.07 (8)
C 25	-0.1701 (2)	-0.7322 (2)	0.2819 (2)	7.8 (1)
C 26	-0.1022 (2)	-0.7709 (3)	0.2810 (2)	9.8 (1)
C 27	-0.0652 (2)	-0.7632 (3)	0.2200 (2)	8.9 (1)
C 28	-0.0944 (2)	-0.7139 (2)	0.1587 (2)	6.07 (9)
C 29	-0.2768 (2)	-0.6386 (2)	0.2242 (2)	6.5 (1)
C 30	-0.2942 (3)	-0.6060 (6)	0.2998 (4)	14.5 (3)

C 31	-0.3306 (2)	-0.7080 (5)	0.1916 (5)	14.0 (2)
C 32	-0.0528 (2)	-0.7048 (4)	0.0908 (2)	8.3 (1)
C 33	-0.0292 (3)	-0.8056 (5)	0.0632 (3)	13.0 (2)
C 34	0.0108 (4)	-0.6390 (4)	0.1047 (4)	12.6 (2)
C 35	0.0950 (1)	-0.1292 (2)	0.3493 (1)	4.30 (7)
C 36	0.1240 (2)	-0.0873 (2)	0.4151 (1)	5.36 (8)
C 37	0.0948 (2)	0.0013 (3)	0.4362 (2)	7.1 (1)
C 38	0.0409 (2)	0.0465 (3)	0.3943 (2)	7.9 (1)
C 39	0.0150 (2)	0.0063 (2)	0.3292 (2)	6.6 (1)
C 40	0.0413 (1)	-0.0817 (2)	0.3050 (1)	4.80 (7)
C 41	0.1857 (2)	-0.1363 (2)	0.4593 (2)	6.9 (1)
C 42	0.1829 (3)	-0.1213 (4)	0.5422 (2)	12.2 (2)
C 43	0.2580 (3)	-0.1038 (4)	0.4350 (3)	11.5 (2)
C 44	0.0142 (2)	-0.1240 (2)	0.2316 (2)	5.55 (8)
C 45	0.0604 (3)	-0.0902 (4)	0.1728 (2)	10.2 (2)
C 46	-0.0650 (2)	-0.1046 (4)	0.2112 (2)	9.1 (1)
H 44	0.017 (2)	-0.194 (2)	0.235 (2)	5.57 (0)
H 8A	-0.140 (1)	-0.500 (2)	0.269 (1)	5.29 (0)
H 10A	-0.004 (2)	-0.484 (2)	0.355 (2)	5.63 (0)
H 16A	-0.274 (2)	-0.374 (3)	-0.080 (2)	8.58 (0)
H 2A	-0.149 (2)	-0.683 (2)	-0.189 (2)	5.99 (0)
H 4A	-0.129 (2)	-0.547 (2)	-0.060 (2)	6.16 (0)
H 4B	-0.177 (2)	-0.633 (2)	-0.061 (2)	6.16 (0)
H 29	-0.281 (2)	-0.571 (2)	0.203 (2)	6.42 (0)
H 25	-0.196 (2)	-0.735 (2)	0.327 (2)	7.74 (0)
H 9A	-0.024 (2)	-0.372 (2)	0.251 (2)	5.46 (0)
H 10B	-0.070 (1)	-0.433 (2)	0.388 (2)	5.63 (0)
H 16B	-0.274 (2)	-0.342 (3)	-0.007 (2)	8.58 (0)
H 3A	-0.193 (2)	-0.483 (2)	-0.168 (2)	5.96 (0)
H 41	0.187 (2)	-0.212 (2)	0.451 (2)	6.92 (0)
H 37	0.118 (2)	0.030 (2)	0.480 (2)	7.11 (0)
H 13A	-0.288 (2)	-0.581 (2)	-0.317 (2)	7.68 (0)
H 15A	-0.353 (2)	-0.561 (3)	-0.056 (2)	8.68 (0)
H 20A	-0.062 (2)	-0.255 (2)	0.467 (2)	7.82 (0)
H 3B	-0.247 (2)	-0.578 (2)	-0.168 (2)	5.96 (0)
H 26	-0.082 (2)	-0.804 (3)	0.322 (2)	9.74 (0)
H 8B	-0.072 (2)	-0.527 (2)	0.232 (2)	5.29 (0)
H 32	-0.085 (2)	-0.683 (2)	0.048 (2)	8.22 (0)
H 46A	-0.074 (2)	-0.032 (3)	0.206 (2)	9.20 (0)
H 19A	0.108 (2)	-0.347 (3)	0.515 (2)	8.94 (0)
H 2B	-0.101 (2)	-0.596 (2)	-0.186 (2)	5.99 (0)
H 46B	-0.078 (2)	-0.144 (3)	0.166 (2)	9.20 (0)
H 20B	-0.055 (2)	-0.203 (3)	0.394 (2)	7.82 (0)
H 43A	0.299 (2)	-0.142 (3)	0.466 (2)	11.54 (0)
H 19B	0.091 (2)	-0.456 (3)	0.478 (2)	8.94 (0)
H 39	-0.024 (2)	0.040 (2)	0.298 (2)	6.60 (0)
H 19C	0.046 (2)	-0.399 (3)	0.525 (2)	8.94 (0)
H 38	0.023 (2)	0.106 (2)	0.413 (2)	7.91 (0)
H 18A	-0.056 (2)	-0.324 (2)	0.120 (2)	7.04 (0)
H 45A	0.042 (2)	-0.117 (3)	0.125 (2)	10.21 (0)
H 13B	-0.263 (2)	-0.628 (2)	-0.385 (2)	7.68 (0)
H 45B	0.110 (2)	-0.102 (3)	0.185 (2)	10.21 (0)
H 18B	-0.047 (2)	-0.405 (3)	0.088 (2)	7.04 (0)
H 17A	-0.204 (2)	-0.287 (2)	0.190 (2)	7.36 (0)
H 18C	-0.103 (2)	-0.334 (2)	0.050 (2)	7.04 (0)
H 14A	-0.138 (2)	-0.464 (3)	-0.376 (2)	8.83 (0)
H 27	-0.022 (2)	-0.787 (3)	0.219 (2)	8.89 (0)
H 43B	0.265 (2)	-0.112 (4)	0.385 (2)	11.54 (0)
H 13C	-0.268 (2)	-0.692 (2)	-0.318 (2)	7.68 (0)
H 17B	-0.249 (2)	-0.366 (3)	0.201 (2)	7.36 (0)
H 9B	-0.092 (2)	-0.330 (2)	0.286 (2)	5.46 (0)

H 15B	-0.352 (2)	-0.536 (3)	0.022 (2)	8.68 (0)
H 14B	-0.179 (2)	-0.436 (3)	-0.309 (2)	8.83 (0)
H 20C	0.001 (2)	-0.182 (2)	0.462 (2)	7.82 (0)
H 34A	0.039 (2)	-0.627 (3)	0.062 (2)	12.40 (0)
H 17C	-0.245 (2)	-0.326 (3)	0.130 (2)	7.36 (0)
H 34B	0.003 (2)	-0.578 (3)	0.127 (2)	12.40 (0)
H 33A	-0.007 (2)	-0.795 (3)	0.016 (2)	12.86 (0)
H 33B	-0.076 (2)	-0.854 (3)	0.052 (2)	12.86 (0)
H 34C	0.039 (3)	-0.678 (4)	0.125 (3)	12.40 (0)
H 33C	0.007 (3)	-0.811 (5)	0.093 (3)	12.86 (0)
H 16C	-0.201 (2)	-0.343 (3)	-0.036 (2)	8.58 (0)
H 14C	-0.100 (2)	-0.453 (3)	-0.300 (2)	8.83 (0)
H 15C	-0.321 (2)	-0.631 (3)	-0.007 (2)	8.68 (0)
H 43C	0.259 (2)	-0.030 (3)	0.456 (2)	11.54 (0)
H 46C	-0.092 (2)	-0.127 (3)	0.254 (2)	9.20 (0)
H 45C	0.052 (2)	-0.022 (3)	0.167 (2)	10.21 (0)
H 42A	0.229 (2)	-0.170 (3)	0.558 (2)	12.22 (0)
H 30A	-0.334 (3)	-0.576 (4)	0.290 (3)	14.40 (0)
H 42B	0.202 (2)	-0.055 (3)	0.546 (3)	12.22 (0)
H 42C	0.147 (3)	-0.154 (4)	0.550 (3)	12.22 (0)
H 31A	-0.327 (2)	-0.756 (4)	0.252 (2)	13.99 (0)
H 31B	-0.361 (3)	-0.693 (5)	0.191 (4)	13.99 (0)
H 30B	-0.273 (3)	-0.587 (6)	0.318 (4)	14.40 (0)

Table 20. Anisotropic Thermal Parameters (Å^2) with Esd's in Parentheses for **11b**

The temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$$

atom	u11	u22	u33	u12	u13	u23
Si1	0.0828 (7)	0.0648 (6)	0.0549 (3)	0.0098 (4)	0.0006 (3)	0.0063 (4)
Si5	0.0786 (5)	0.0618 (6)	0.0519 (3)	0.0092 (4)	-0.0076 (3)	-0.0045 (4)
Si7	0.0708 (5)	0.0525 (5)	0.0532 (3)	-0.0060 (4)	0.0002 (3)	-0.0052 (3)
Si11	0.0805 (5)	0.0776 (6)	0.0429 (3)	-0.0258 (4)	0.0023 (3)	0.0020 (4)
N 21	0.062 (1)	0.050 (1)	0.055 (1)	0.002 (1)	-0.000 (1)	-0.002 (1)
N 22	0.060 (1)	0.058 (1)	0.048 (1)	-0.002 (1)	0.0019 (9)	0.005 (1)
C 2	0.094 (2)	0.076 (2)	0.056 (2)	0.018 (2)	0.001 (2)	-0.003 (2)
C 3	0.099 (2)	0.074 (2)	0.052 (2)	0.022 (2)	-0.001 (2)	-0.004 (2)
C 4	0.099 (2)	0.081 (2)	0.053 (2)	0.018 (2)	-0.002 (2)	-0.002 (2)
C 6	0.054 (2)	0.051 (2)	0.051 (1)	0.002 (1)	0.002 (1)	-0.002 (1)
C 8	0.079 (2)	0.062 (2)	0.058 (2)	-0.017 (2)	-0.003 (1)	-0.004 (1)
C 9	0.084 (2)	0.068 (2)	0.054 (2)	-0.021 (2)	-0.006 (1)	0.001 (2)
C 10	0.081 (2)	0.075 (2)	0.057 (2)	-0.022 (2)	-0.003 (1)	0.006 (2)
C 12	0.062 (2)	0.057 (2)	0.039 (1)	-0.003 (1)	-0.008 (1)	0.004 (1)
C 13	0.080 (2)	0.120 (3)	0.090 (2)	0.020 (2)	-0.006 (2)	0.001 (2)
C 14	0.152 (4)	0.072 (2)	0.113 (3)	0.019 (2)	0.022 (3)	0.014 (2)
C 15	0.083 (3)	0.149 (4)	0.093 (3)	-0.009 (3)	-0.028 (2)	-0.005 (3)
C 16	0.162 (4)	0.074 (3)	0.084 (2)	0.036 (2)	-0.023 (3)	0.006 (2)
C 17	0.109 (3)	0.081 (3)	0.088 (2)	0.021 (2)	-0.003 (2)	-0.028 (2)
C 18	0.099 (3)	0.088 (3)	0.081 (2)	-0.024 (2)	0.005 (2)	0.009 (2)
C 19	0.143 (4)	0.136 (3)	0.057 (2)	-0.056 (3)	-0.019 (2)	0.027 (2)

C 20	0.101 (3)	0.110 (3)	0.092 (2)	-0.031 (2)	0.045 (2)	-0.029 (2)
C 23	0.062 (2)	0.043 (1)	0.060 (2)	0.003 (1)	0.007 (1)	0.002 (1)
C 24	0.073 (2)	0.048 (2)	0.072 (2)	0.006 (1)	0.017 (1)	0.010 (1)
C 25	0.120 (3)	0.092 (2)	0.087 (2)	0.033 (2)	0.041 (2)	0.034 (2)
C 26	0.132 (3)	0.147 (4)	0.094 (3)	0.074 (3)	0.030 (2)	0.059 (2)
C 27	0.101 (3)	0.144 (3)	0.096 (2)	0.060 (2)	0.028 (2)	0.047 (2)
C 28	0.073 (2)	0.086 (2)	0.072 (2)	0.026 (2)	0.014 (2)	0.019 (2)
C 29	0.072 (2)	0.085 (2)	0.090 (2)	0.009 (2)	0.024 (2)	0.013 (2)
C 30	0.120 (4)	0.259 (7)	0.171 (6)	0.062 (5)	0.032 (4)	-0.094 (4)
C 31	0.084 (3)	0.161 (5)	0.284 (7)	-0.015 (4)	-0.007 (4)	-0.068 (4)
C 32	0.083 (3)	0.150 (4)	0.083 (2)	0.044 (3)	0.026 (2)	0.024 (2)
C 33	0.153 (5)	0.202 (6)	0.143 (4)	-0.024 (5)	0.067 (4)	-0.071 (4)
C 34	0.186 (6)	0.124 (4)	0.177 (6)	0.009 (4)	0.114 (5)	0.013 (4)
C 35	0.060 (2)	0.053 (2)	0.050 (1)	-0.008 (1)	0.010 (1)	0.001 (1)
C 36	0.080 (2)	0.069 (2)	0.054 (2)	-0.014 (2)	0.006 (1)	-0.001 (1)
C 37	0.117 (3)	0.084 (2)	0.069 (2)	-0.013 (2)	0.008 (2)	-0.023 (2)
C 38	0.120 (3)	0.083 (3)	0.100 (3)	0.013 (2)	0.019 (2)	-0.024 (2)
C 39	0.089 (2)	0.073 (2)	0.090 (2)	0.015 (2)	0.010 (2)	-0.006 (2)
C 40	0.062 (2)	0.057 (2)	0.063 (2)	-0.002 (1)	0.007 (1)	0.002 (1)
C 41	0.106 (3)	0.090 (2)	0.063 (2)	-0.018 (2)	-0.021 (2)	0.005 (2)
C 42	0.204 (6)	0.181 (6)	0.073 (2)	-0.049 (4)	-0.035 (3)	0.015 (3)
C 43	0.090 (3)	0.194 (5)	0.150 (4)	-0.002 (4)	-0.019 (3)	0.050 (4)
C 44	0.078 (2)	0.065 (2)	0.066 (2)	0.002 (2)	-0.014 (1)	0.001 (2)
C 45	0.146 (4)	0.178 (4)	0.066 (2)	-0.024 (4)	0.015 (2)	-0.012 (3)
C 46	0.097 (3)	0.131 (4)	0.116 (3)	0.010 (3)	-0.033 (2)	-0.005 (3)

Table 21. Intramolecular Distances (Å) with Esd's in Parentheses for **11b**

atom	atom	distance	atom	atom	distance
Si1	- C 13	1.856 (4)	C 23	- C 24	1.398 (4)
Si1	- C 14	1.867 (4)	C 24	- C 25	1.386 (4)
Si1	- C 2	1.870 (3)	C 24	- C 29	1.517 (4)
Si5	- C 15	1.858 (4)	C 25	- C 26	1.370 (6)
Si5	- C 16	1.860 (4)	C 26	- C 27	1.361 (6)
Si5	- C 4	1.867 (3)	C 27	- C 28	1.386 (5)
Si5	- C 6	1.915 (2)	C 28	- C 32	1.519 (5)
Si7	- C 17	1.853 (4)	C 29	- C 31	1.473 (7)
Si7	- C 18	1.859 (4)	C 29	- C 30	1.514 (8)
Si7	- C 8	1.875 (3)	C 32	- C 34	1.493 (8)
Si7	- C 6	1.914 (2)	C 32	- C 33	1.543 (8)
Si11	- C 20	1.862 (4)	C 35	- C 40	1.399 (3)
Si11	- C 19	1.867 (4)	C 35	- C 36	1.407 (3)
Si11	- C 10	1.872 (3)	C 36	- C 37	1.393 (5)
Si11	- C 12	1.917 (2)	C 36	- C 41	1.511 (4)
N 21	- C 6	1.286 (3)	C 37	- C 38	1.365 (5)
N 21	- C 23	1.422 (3)	C 38	- C 39	1.369 (5)
N 22	- C 12	1.289 (3)	C 39	- C 40	1.384 (4)
N 22	- C 35	1.424 (3)	C 40	- C 44	1.516 (4)
C 2	- C 3	1.527 (4)	C 41	- C 43	1.515 (6)
C 3	- C 4	1.530 (4)	C 41	- C 42	1.540 (5)
C 8	- C 9	1.535 (4)	C 44	- C 45	1.502 (6)
C 9	- C 10	1.535 (4)	C 44	- C 46	1.516 (5)
C 23	- C 28	1.392 (4)			

Table 22. Intermolecular Distances (Å) with Esd's in Parentheses for **11b**

atom	atom	adc	distance
Si1	- C 12	(2)	1.918 (2)

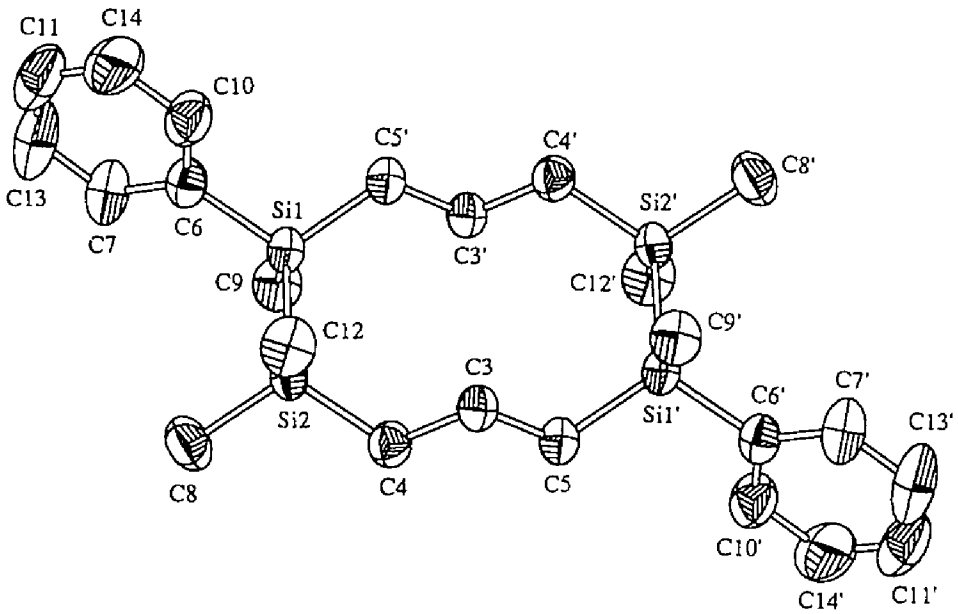
Table 23. Intramolecular Angles (deg) with Esd's in Parentheses for **11b**

atom	atom	atom	angle	atom	atom	atom	angle
C 13	- Si1	- C 14	108.0 (2)	C 24	- C 23	- N 21	119.9 (2)
C 13	- Si1	- C 2	111.3 (2)	C 25	- C 24	- C 23	117.6 (2)
C 14	- Si1	- C 2	109.2 (2)	C 25	- C 24	- C 29	121.0 (3)
C 15	- Si5	- C 16	109.6 (2)	C 23	- C 24	- C 29	121.3 (2)
C 15	- Si5	- C 4	111.5 (2)	C 26	- C 25	- C 24	121.4 (3)
C 15	- Si5	- C 6	107.4 (1)	C 27	- C 26	- C 25	120.2 (4)
C 16	- Si5	- C 4	109.2 (2)	C 26	- C 27	- C 28	120.8 (3)
C 16	- Si5	- C 6	114.6 (1)	C 27	- C 28	- C 23	118.6 (3)
C 4	- Si5	- C 6	104.4 (1)	C 27	- C 28	- C 32	120.8 (3)
C 17	- Si7	- C 18	109.1 (2)	C 23	- C 28	- C 32	120.6 (2)
C 17	- Si7	- C 8	108.9 (1)	C 31	- C 29	- C 30	112.1 (4)
C 17	- Si7	- C 6	107.2 (1)	C 31	- C 29	- C 24	110.2 (3)
C 18	- Si7	- C 8	109.7 (1)	C 30	- C 29	- C 24	113.0 (3)
C 18	- Si7	- C 6	105.8 (1)	C 34	- C 32	- C 28	110.8 (4)
C 8	- Si7	- C 6	116.0 (1)	C 34	- C 32	- C 33	110.7 (4)
C 20	- Si11	- C 19	109.2 (2)	C 28	- C 32	- C 33	111.7 (4)
C 20	- Si11	- C 10	107.4 (1)	C 40	- C 35	- C 36	121.4 (2)
C 20	- Si11	- C 12	117.3 (1)	C 40	- C 35	- N 22	119.4 (2)
C 19	- Si11	- C 10	110.6 (2)	C 36	- C 35	- N 22	119.0 (2)
C 19	- Si11	- C 12	105.7 (2)	C 37	- C 36	- C 35	117.4 (2)
C 10	- Si11	- C 12	106.5 (1)	C 37	- C 36	- C 41	122.2 (2)
C 6	- N 21	- C 23	124.0 (2)	C 35	- C 36	- C 41	120.4 (2)
C 12	- N 22	- C 35	122.3 (2)	C 38	- C 37	- C 36	121.5 (3)
C 3	- C 2	- Si1	116.3 (2)	C 37	- C 38	- C 39	120.4 (3)
C 2	- C 3	- C 4	112.8 (2)	C 38	- C 39	- C 40	121.2 (3)
C 3	- C 4	- Si5	117.4 (2)	C 39	- C 40	- C 35	118.1 (2)
N 21	- C 6	- Si7	129.2 (2)	C 39	- C 40	- C 44	120.9 (2)
N 21	- C 6	- Si5	106.8 (2)	C 35	- C 40	- C 44	120.9 (2)
Si7	- C 6	- Si5	124.0 (1)	C 36	- C 41	- C 43	111.5 (3)
C 9	- C 8	- Si7	113.6 (2)	C 36	- C 41	- C 42	113.0 (3)
C 8	- C 9	- C 10	112.9 (2)	C 43	- C 41	- C 42	110.3 (4)
C 9	- C 10	- Si11	114.3 (2)	C 45	- C 44	- C 40	110.5 (3)
N 22	- C 12	- Si11	128.6 (2)	C 45	- C 44	- C 46	111.4 (3)
C 28	- C 23	- C 24	121.2 (2)	C 40	- C 44	- C 46	113.9 (3)
C 28	- C 23	- N 21	118.7 (2)				

Table 24. Intermolecular Angles (deg) with Esd's in Parentheses for **11b**

atom	atom adc	atom adc	angle	atom	atom adc	atom adc	angle
C 13	- Si1 (1)	- C 12 (2)	106.7 (1)	N 22	- C 12 (1)	- Si1 (2)	107.3 (2)
C 14	- Si1 (1)	- C 12 (2)	114.8 (2)	Si11	- C 12 (1)	- Si1 (2)	124.0 (1)
C 2	- Si1 (1)	- C 12 (2)	106.8 (1)				

Figure 4. Crystal Structure of (1*R**,6*S**)-Isomer of **3b2**



Crystal Data for (1*R**,6*S**)-**3b2**: crystal size 0.45 × 0.50 × 0.55 mm; monoclinic, space group *P21/c* (no. 14), $Z = 2$; $a = 7.686$, $b = 27.867$, $c = 6.829$ Å; $\beta = 110.43°$; $V = 1371$ Å^3, $\rho_{calcd} = 1.07$ g/cm^3; max. $2\theta = 135°$ (Cu Kα, $\lambda = 1.54178$ Å, graphite monochromator, $\omega/2\theta$-Scan, $T = 293$ K); 2585 reflections measured, 2285 independent, 2108 included in the refinement, Lorentzian polarization; direct method, anisotropical refinement for non-hydrogen atoms by full-matrix least-squares against $|F|$ with program package CrystanG (Mac Science), 147 parameters; $R = 0.080$, $R_W = 0.122$. All hydrogen atoms were included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters.

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Chapter 3

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submitted

Chapter 4

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Other Publications

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Shono, T.; Kise, N.; Oike, H.; Yoshimoto, M.; Okazaki, E. *Tetrahedron Lett.* **1992**, *33*, 5559–5562.

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